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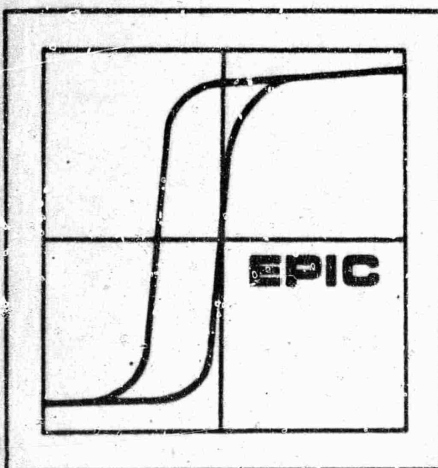
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# LEAD SULFIDE

M. NEUBERGER

DATA SHEET DS-150

NOVEMBER 1966



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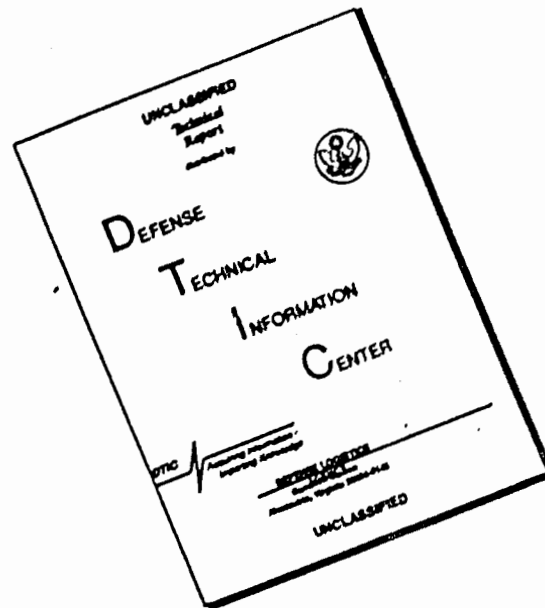
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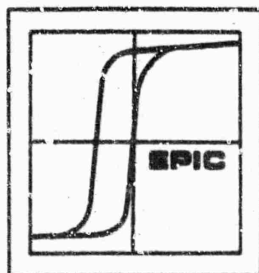
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## FOREWORD

This report was prepared by Hughes Aircraft Company, Culver City, California, under Contract Number AF 33(615)-2460. The contract was initiated under Project No. 7381, "Materials Application," Task No. 738103, "Materials Information Development, Collection, and Processing." The work was administered under the direction of the Air Force Materials Laboratory, Research and Technology Division, Air Force Systems Command, Wright-Patterson Air Force Base, Ohio, with Mr. R. F. Klinger, Project Engineer.

The Electronic Properties Information Center conducts documentary research based on the collection, analysis, and review of the scientific and technical literature relevant to the electrical, electronic, and magnetic properties of materials. The primary objective of this program of evaluation and correlation is to provide a source of competent information to the DoD community. By means of several series of publications such as Data Sheets, Special Reports, Interim Reports and several services such as Computer Bibliographies, technical question answering services, and special studies, research and development support is made available to this extended community.

The initial step in the preparation of this data sheet was retrieval, by means of a modified coordinate index, of all lead sulfide literature in the EPIC file. Bibliographies were also reviewed to ensure the inclusion of all relevant literature. Papers containing primary experimental data were selected. Secondary reviews and evaluations were considered during the data analysis.

If data available from several sources are judged to be equally

valid, then all are given. Data are considered questionable and rejected for inclusion because of faulty or dubious measurements, unknown sample composition, or if more reliable and inclusive data are available from another source. Selection of data is based upon evaluation of that which is most representative, precise, reliable and inclusive over a wide range of parameters.

Within every property section we have tried to include every available parameter and range of experimental condition found in the literature. Measurement environment and sample specification are included when available. Some alterations in units and presentation may be made to facilitate comparison with other experimental data.

This report consists of the compiled data sheets on lead sulfide. A full list of EPIC publications to-date appears at the end of the report.

The author wishes to acknowledge the assistance afforded by Dr. J. J. Grossman in reviewing the experimental data, and the contribution of Dr. Sheldon Welles in the review of the compilation. The supporting assistance of another member of the EPIC staff, Mrs. Marjorie Dunn, is gratefully acknowledged.



## ABSTRACT

These data sheets present a compilation of a wide range of electronic properties for lead sulfide. Electrical properties include conductivity, dielectric constant, Hall coefficient, and mobility. Emission data have been broken down into the varied electron and photon emissions which result from application of electromagnetic energy over a wide spectrum and a wide variety of photoelectronic phenomena is shown. Energy data include energy bands, energy gap, and energy levels, as well as effective mass tables, and work function. The optical properties include absorption, reflection, and refractive index. Magnetic data are presented, as well as several other physical phenomena, such as Debye temperature. Thermoelectric and thermomagnetic properties are shown. Each property is compiled over the widest possible range of parameters including bulk and film form, from references obtained in a thorough literature search.

A summary of crystal structure and phase transitions has been included.

This report has been reviewed and is approved for publication.



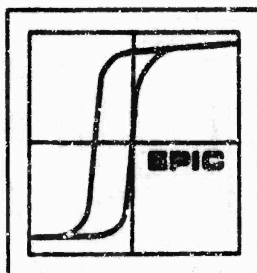
Emil Schafer, Head  
Electronic Properties Information Center

  
John W. Atwood  
Project Manager



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### SUMMARY

Galena, the natural lead sulfide, is the most important lead mineral and one of the most widely distributed sulfide minerals, occurring in both sedimentary and hydrothermal vein deposits. It is found with many other iron and silver ores as well as with various silicates.

The natural ore is often obtained in very pure form and is so used in the laboratory as will be noted in these data sheets.

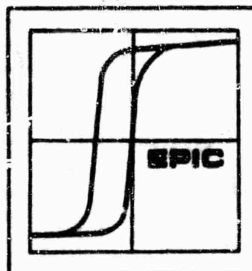
The mineral name of lead sulfide, galena, is also the family name for the lead chalcogenides including manganese and calcium sulfide. These minerals are face centered cubic with the halite structure. <sup>4,1</sup>

### Lattice Parameters <sup>2</sup>

$$\begin{aligned} a_0 &= 5.9362 \text{ \AA} \text{ at } 26^\circ\text{C} \\ &5.92 \pm 3 \text{ \AA} \quad (\text{natural galena}) \\ &5.9360 \pm 4 \text{ \AA} \quad (\text{natural galena, very pure}) \\ &5.94 \text{ \AA} \quad (\text{natural galena}) \end{aligned}$$

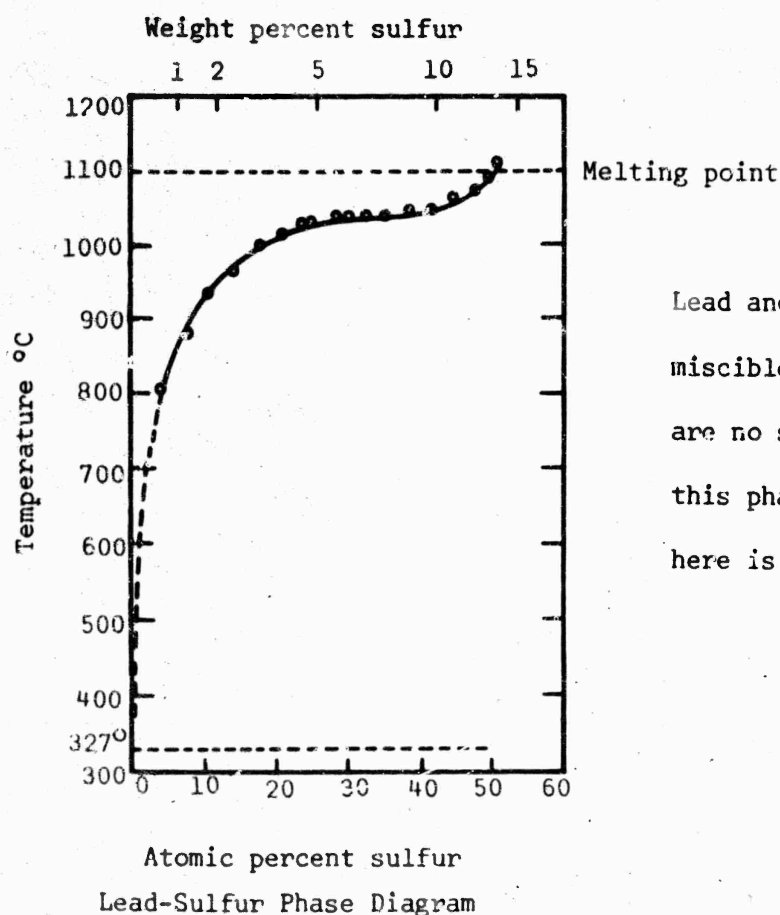
Galena is generally cubic or cubo-octahedral and tabular on (001). This is the cleavage plane and cleavage is easy and highly perfect. The mineral is generally found in massive growths and twinning is common. It is very soft and heavy; hardness = 2.5-2.75 on the Mohs scale and specific gravity = 7.58 g/cm<sup>3</sup>. It has metallic lustre and is opaque; in polished sections it is isotropic under polarized light. The melting point is 1115°C. <sup>4</sup>

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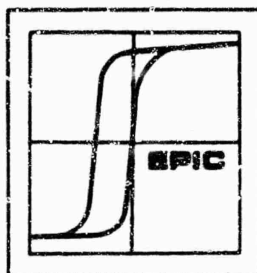
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Lead and lead sulfide are completely miscible in the liquid state and there are no sub-sulfides, as may be seen in this phase diagram. The melting point here is given as  $1119 \pm 16^\circ\text{C}$ .<sup>3</sup>

Lead sulfide is widely employed as a detector in infrared systems. These devices are highly responsive in the visible and infrared regions; at  $25^\circ\text{C}$  the radiation range is from 0.4 to 3.3 microns. As the temperature decreases the wavelength limit moves further into the IR so that at liquid nitrogen ( $77^\circ\text{K}$ ) there is a response at 4.3 microns [Ref. 3768]. The spectral response of films may be displaced toward shorter wavelengths by oxygen doping, reaching 1.5 microns at room temperature [Ref. 3889, 22736]. Oxygen has another sensitizing effect on these films by converting n-type to the more responsive p-type. It should also be noted that chemically deposited films are more homogeneous and reproducible than evaporative layers [Ref. 22736].

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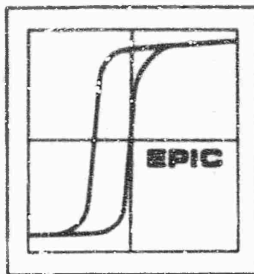
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Small deviations from stoichiometry caused by slight differences of temperature and pressure during preparation have large effect on the electronic as well as the physical properties of both the crystals and films, by introducing vacancy defects. In films these defects may be annealed out by careful heating. At a given dopant level, the heat treatment increases resistivity with consequent decrease in lifetime and a net increase in response. Excessive heat however, will destroy response [Ref. 22736].

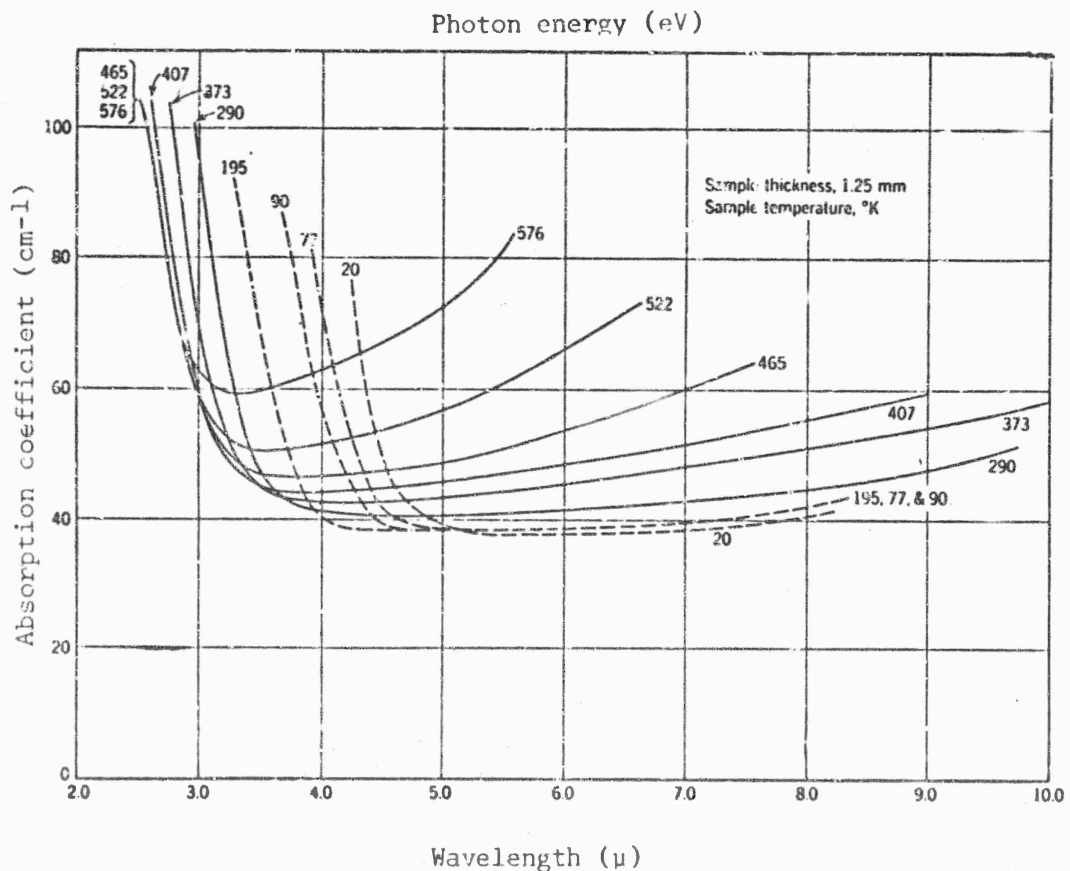
- <sup>1</sup> Wyckoff, Ralph W.G. Crystal Structures, v. 1, 2nd Ed. Inters. Ci., 1963.
- <sup>2</sup> Donnay, J.D.H. Crystal Data. Determinative Tables. 2nd Ed. American Crystallography Association, 1963.
- <sup>3</sup> Hansen, M. Constitution of Binary Alloys. 2nd Ed. Prepared with the cooperation of Anderko, K. N.Y., McGraw-Hill, 1958. p. 1100.
- <sup>4</sup> Dana, J.D. The System of Mineralogy of James Dwight Dana and Edward Salisbury Dana. Yale University, 1837-1892. v. 1, 7th ed. Entirely rewritten and greatly enlarged by Palache, C., et al. N.Y., Wiley, 1944. p. 200-204.





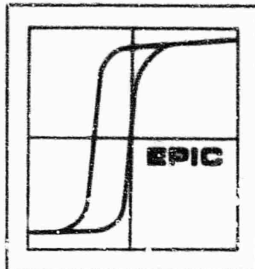
# LEAD SULFIDE

## ABSORPTION



Absorption coefficient as a function of photon energy for single crystal, n-type lead sulfide at temperatures from 20-590°K. Curves are calculated from transmission data, and those taken below 300°K are shown by dotted lines. Carrier concentration may vary from  $10^{17}$  to  $10^{20}$  cm<sup>-3</sup>, but type and carrier concentration do not affect the edge. The absorption edge coincides with the long wavelength limit of photoconductivity and beyond the photo conductivity limit, the absorption coefficient is small and in part, due to the free carriers.

[Ref. 3768]

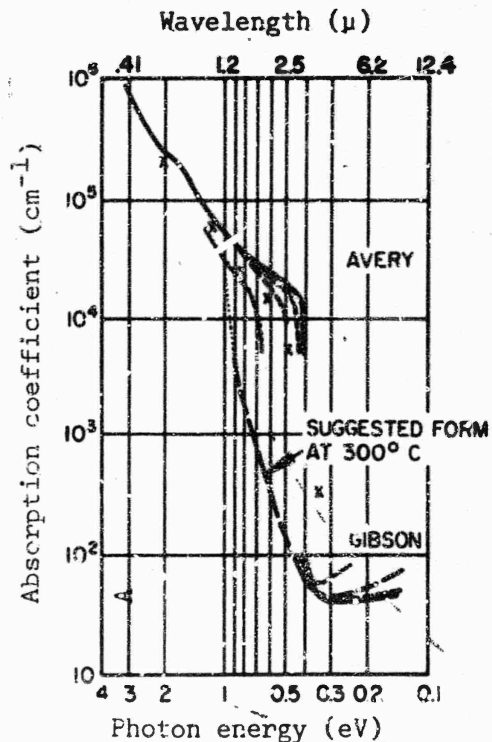


## LEAD SULFIDE

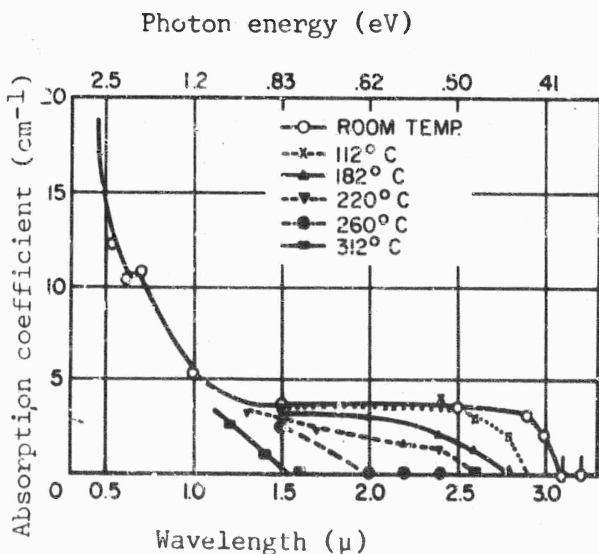
### ABSORPTION

Absorption coefficient as a function of photon energy in single crystal lead sulfide. Both natural and synthetic crystal cleavage faces were used. The absorption coefficient is calculated from optical measurements of transmission or reflection and indicates the predominant importance of temperature.

- 20° C
  - - - 108° C (AVERY) & 100° C (GIBSON)
  - · - 135° C (AVERY) & 192° C (GIBSON)
  - · - 295° C (AVERY) & 303° C (GIBSON)
  - · · 330° C
  - x VERNIER [Ref. 11580]
- [Ref. 3444]



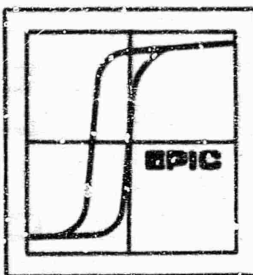
[Ref. 3452]



Absorption coefficient as a function of wavelength at various temperatures, for lead sulfide. The absorption coefficient is calculated as the imaginary part of the dielectric constant ( $2n^2k$ ). It is plotted as a function of photon energy in single crystal lead sulfide at temperatures from 20-312°C.

[Ref. 3452]



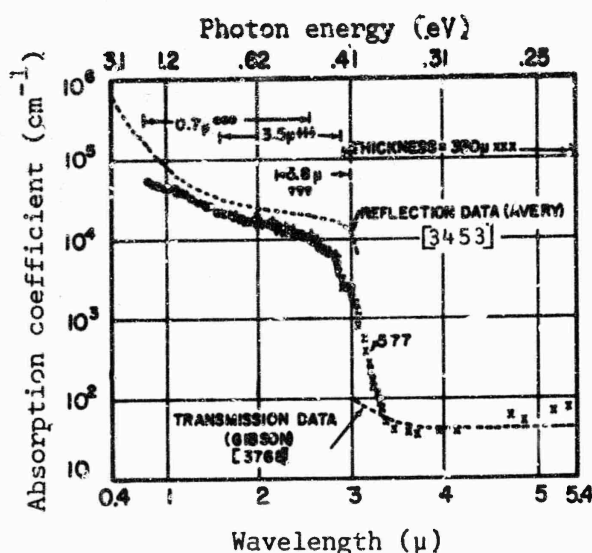


## LEAD SULFIDE

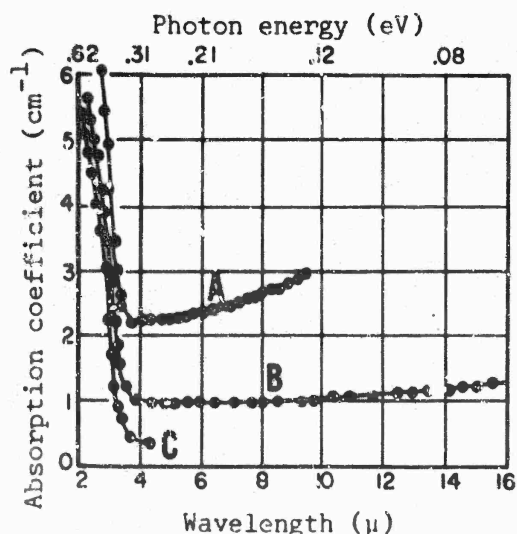
### ABSORPTION

Absorption coefficient as a function of photon energy for single crystal lead sulfide cleaved on (100). Both natural and synthetic crystals were used,  $n = 10^{17}$  to  $10^{19}$   $\text{cm}^{-3}$ . Crystal thickness varied from 0.7 to 350  $\mu$  and corrections were made for reflectivity.

• } Data taken at four  
+ } sample thicknesses.  
x }  
v }



[Ref. 577]



Absorption coefficient, as a function of photon energy for 3 cleaved lead sulfide single crystal (100) planes. The absorption coefficient is calculated from the transmission corrected for reflectivity ( $R=0.36$ ):

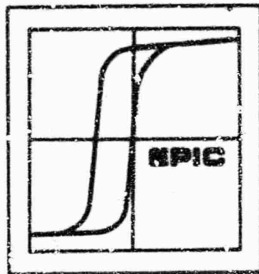
$$\alpha = \log \frac{I_0 (1-R)^2}{I} \times \frac{2.3}{\chi}$$

$I_0$  = incident illumination  
 $I$  = transmitted illumination  
 $\chi$  = is the sample thickness

Thicknesses  
A 1600  $\mu$   
B 500  
C 190

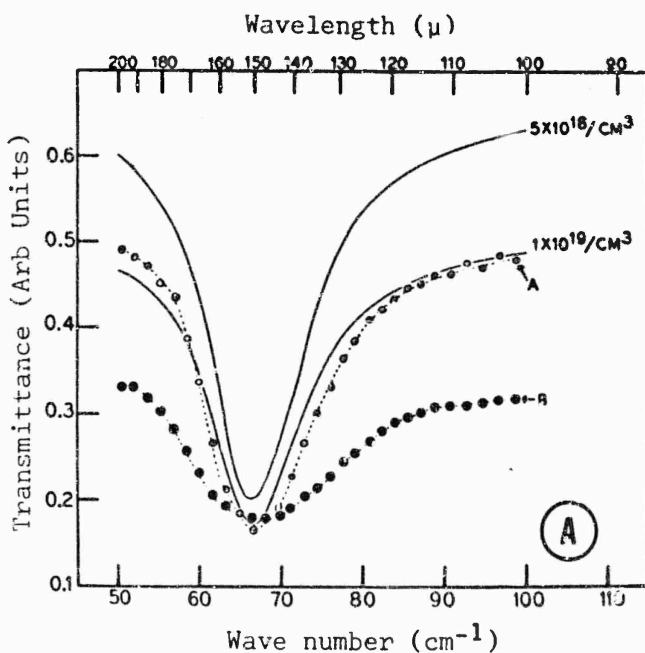
Variation due to thickness is slight.

[Ref. 3768]



## LEAD SULFIDE

### ABSORPTION



A. Transmittance as a function of infrared wavelength for two epitaxial single crystal lead sulfide films at 300°K. Sample thickness 180-500 Å.

— Theoretical curve calculated for:  
Mobility = 350 cm<sup>2</sup>/Vsec  
Effective mass = 0.10 m<sub>0</sub>  
Optical dielectric constant = 17.3  
Static dielectric constant = 174.4  
Two carrier concentrations  
n = 5x10<sup>18</sup>cm<sup>-3</sup>  
n = 1x10<sup>19</sup>cm<sup>-3</sup>

A ○ Grown on heated substrate and normalized to coincide with theoretical curve for 10<sup>19</sup>cm<sup>-3</sup> at 300°K.

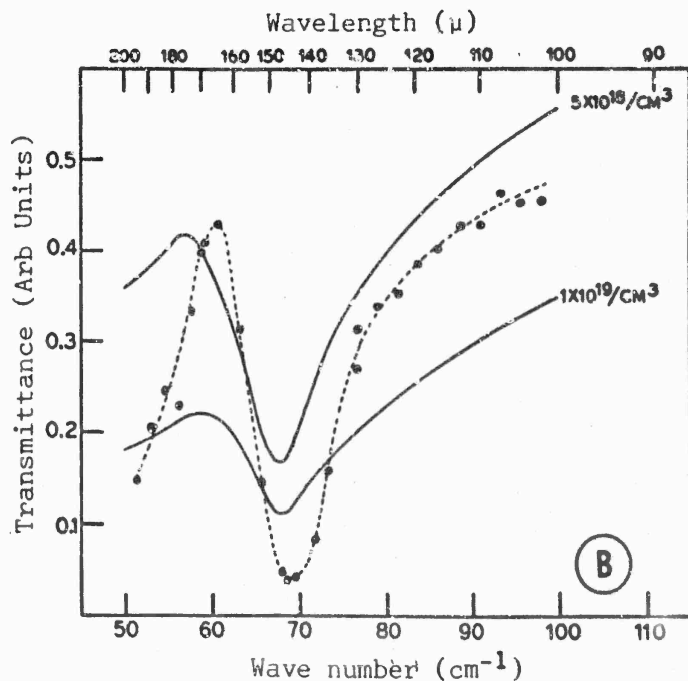
B ● Grown on cold substrate and also normalized. [Ref. 24929]

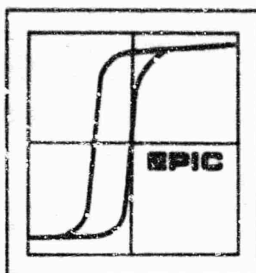
B. Transmittance as a function of infrared wavelength for film A (above) at 77°K.

— Theoretical curves calculated as above but for a mobility of 3500 cm<sup>2</sup>/Vsec.

Low temperature measurements show minimum at long wavelengths due to free carriers. These data indicate a static dielectric constant = 174.4

[Ref. 24929]



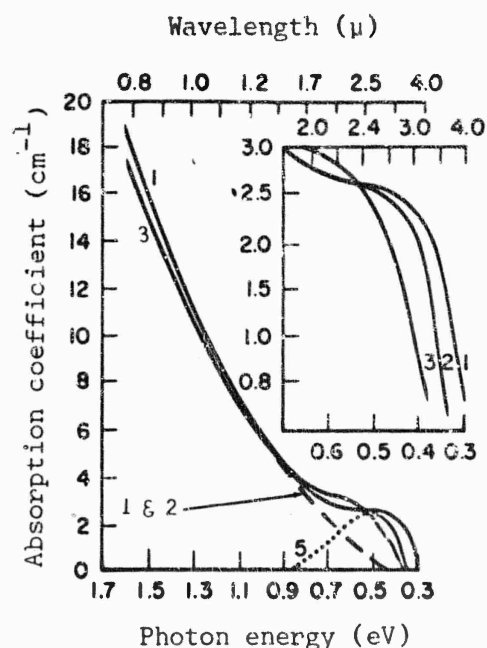


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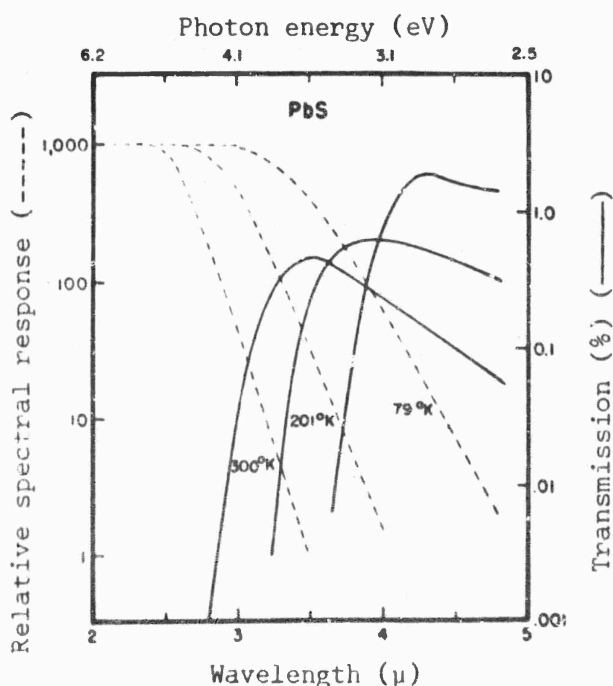
### ABSORPTION

Absorption coefficient as a function of photon energy for films and single crystals of lead sulfide. 1)-Film with small-grain structure 2)-Film with large-grain structure; 3)-Single crystal; [3453]; 5)-Exciton absorption curve. The inset enlarges the curves from 0.7 to 0.3 eV. Curves are calculated from transmission and reflection data taken on chemically produced films.

Above  $3.2\mu$  the films show additional absorption which is greater in reflecting mirror-like films and less in rougher grained structures. This is probably due to increase in structural defects.

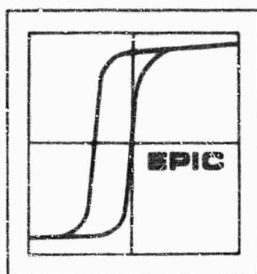


[Ref. 19776]



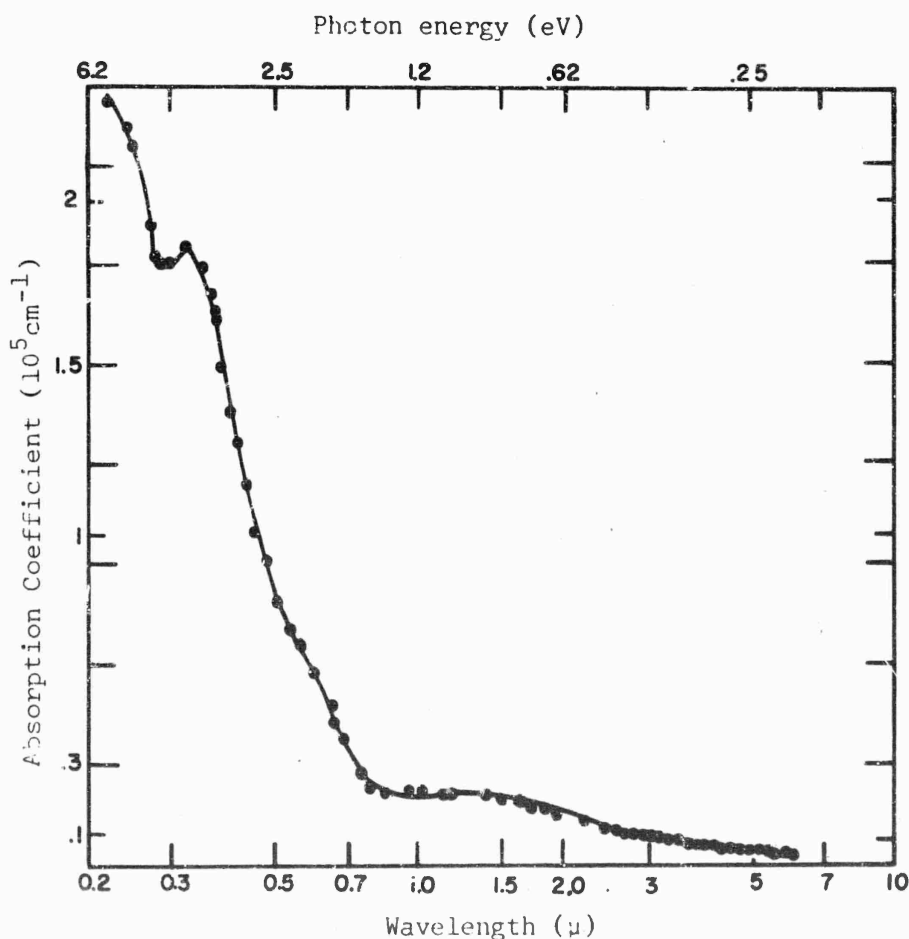
Transmission of lead sulfide single crystal, thickness 48 microns. Relative spectral response of lead sulfide photocells. Curves show shift in maximum with temperature. For a section of this thickness there is considerable variation in transmission with change in wavelength of illumination.

[Ref. 7815]



LEAD SULFIDE

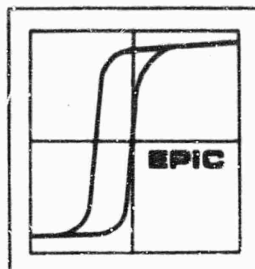
ABSORPTION



The absorption coefficient as a function of photon energy in chemically deposited lead sulfide films at 300°K. [Ref. 3444]

The data taken here covers a wide range of the spectrum from infra-red to ultra-violet and shows several of the energy states given in the energy band structure in Refs. (13554 and 22572). The most apparent result is a large rise in absorption at 1.3 eV. This corresponds to the smallest vertical transition as shown on page 41. The rise in absorption at 4.6 eV corresponds to the transition between the top of the full s-band  $\Gamma_1$  at 2.73 eV to the top of the  $K_1$  band at 1.56 eV seen on the same graph. A marked band extends from 1 to 6 microns at an absorption coefficient of about  $10^4 \text{ cm}^{-1}$ , and is apparently a result of film defects.

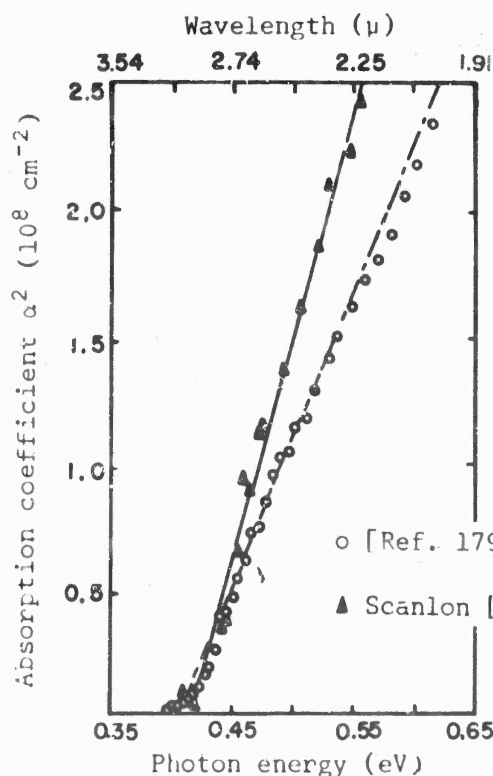
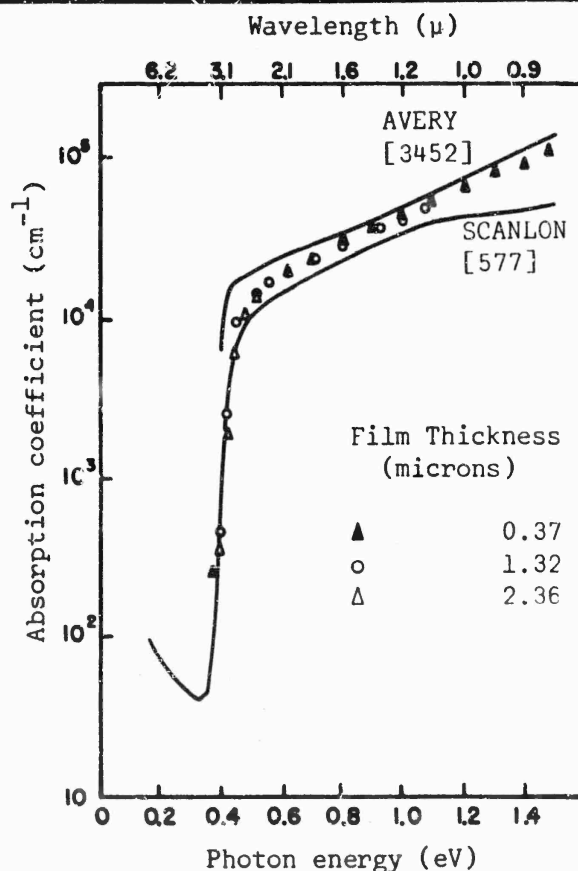




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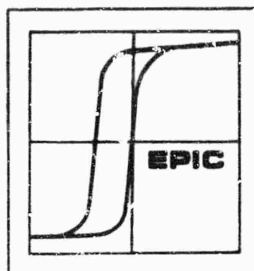
### ABSORPTION

The absorption coefficient as a function of photon energy of single-crystal lead sulfide films at 300°K. The two solid curves represent the results of Avery and Scanlon. The experimental points indicate that film thickness may vary from 0.37 to 2.36 microns without effect on the absorption coefficient.



The absorption coefficient squared as a function of photon energy in single crystal lead sulfide films at 300°K.

[Ref. 17982]

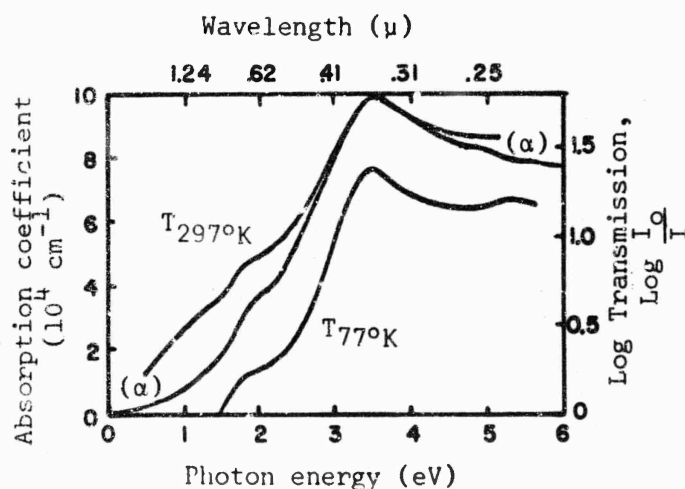


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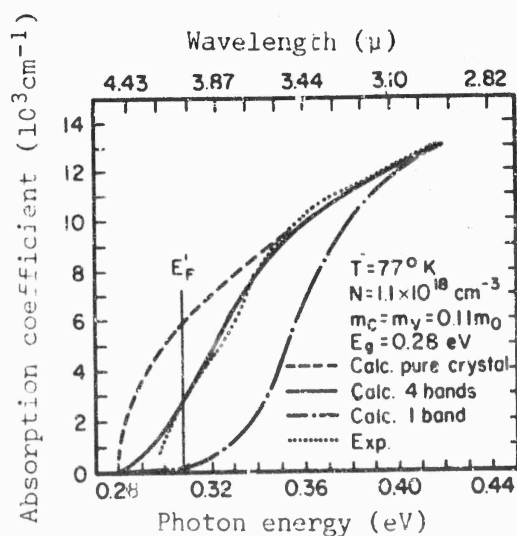
## ABSORPTION

Absorption coefficient and log transmission as a function of photon energy for a lead sulfide film at 77°K and 297°K. This is an epitaxial single crystal film, .034 microns thick. The absorption coefficient curve  $\alpha$  is calculated for 300°K from reflectivity data.

$I_0$  is incident illumination  
 $I$  is transmitted illumination



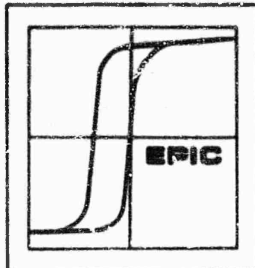
[Ref. 14189]



The measured optical absorption edge in epitaxial single crystal lead sulfide at 77°K showing the Burstein-Moss shift. Calculated curves for the absorption coefficient are shown assuming the free carriers to be in one parabolic and spherical band located at  $\Gamma$  or in four equivalent parabolic and spherical bands located at L. (See ENERGY BANDS)

[Ref. 16127]

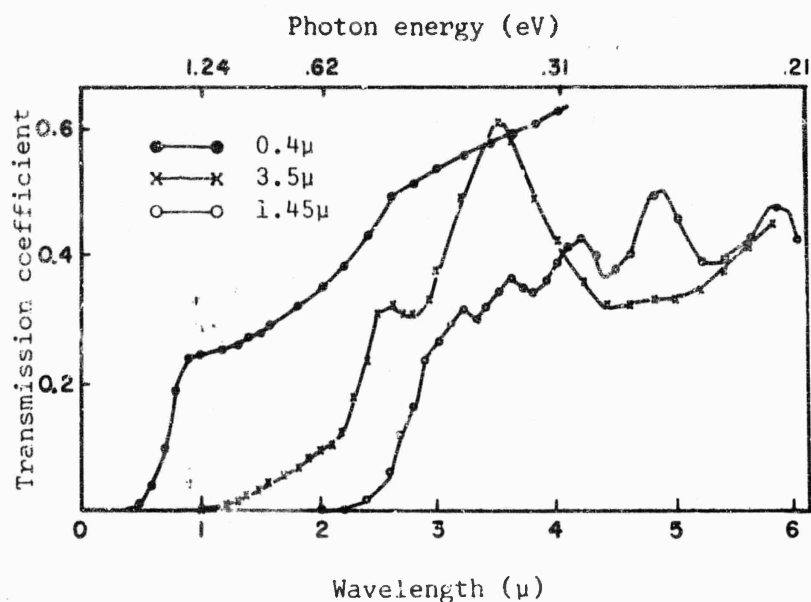




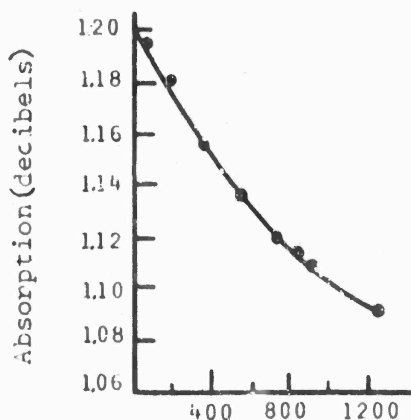
# LEAD SULFIDE

## ABSORPTION

Transmission as a function of wavelength in chemically deposited lead sulfide films of three thicknesses.



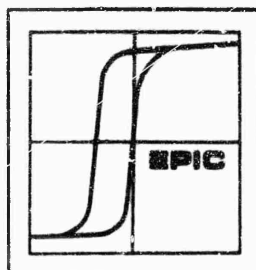
[Ref. 11580]



The absorption of 10 Gc electromagnetic radiation as a function of the magnitude of voltage applied to a lead sulfide film on a mica substrate.  $E_{av}$  is the field strength in V/cm sample length. The decrease in absorption on application of an external electric field is due to tendency for the electron drift velocity to saturate at high electric fields.

[Ref. 13988]

Field strength,  $E_{av}$  (V/cm)



# LEAD SULFIDE

## CARRIER DIFFUSION

Effective diffusion length in chemically deposited lead sulfide films at various temperatures, and flux intensities.

$L_x$ ( $10^{-6}$ cm)	Flux ( $10^{14}$ photons/sec)	Method	Temperature °K	Ref.
4.2	8.5	Photoelectro-magnetic measurements at 9kGauss	187	7700
6.0	8.5		192	
4.0	8.5		193	
5.5	14.5		193	
7.5	5.25		193	
4.0	4.0		193	
2.2	11.5		225	
1.9	7.0		225	
4.0	3.2		225	
5.5	1.9		225	
2.5	7.75		297	
4.0	3.50		297	
4.2	2.15		297	
4.5	1.0		297	
4.2	0.35		297	
6.0	2.2		298	
3.2	13		314	
4.2	8.0		314	
4.5	3.5		314	

The effective diffusion length  $L_x$  is calculated from the recombination velocity

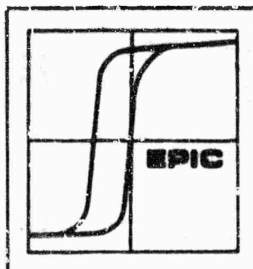
$$V_s = \frac{2 \phi B L_x \times 10^{-8}}{N_p dW}$$

, the denominator represents the hole carrier concentration times sample dimensions. The diffusion length  $L$  may also be calculated from  $(D\tau)^{1/2}$ .

Film thickness is about .5 microns.

[Ref. 7700]

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# LEAD SULFIDE

## CARRIER DIFFUSION

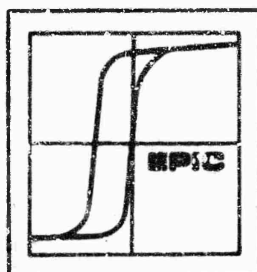
Symbol	Value ( $10^{-6}$ cm)	Sample	Method	Temperature °K	Ref.
L	1.	This diffusion length is associated with a lifetime $\tau = 8$ microsec	Photovoltaic	300	290

$L_x$ ( $10^{-6}$ cm)	Flux ( $10^{14}$ photons/sec)	Wavelength ( $\mu$ )	Test Measurement	Temperature °K	Ref.
.26	11.0	2.1	PEM*	293	7700
.23	2.0	2.1	at 10kGauss	293	
.067	3.5	1.25		295	
.076	1.25	1.25		295	
.29	11.0	2.1		196	
.28	2.0	2.1		196	
.05	3.5	1.25		194	
.05	1.1	1.25		194	
.05	4.7	1.25		195	
.05	3.0	1.25		195	

\*Photoelectro-magnetic

The effective diffusion length is essentially independent of temperature and light intensity. The change in  $L_x$  with wavelength is not large but it is larger for the longer wavelength. The minority carrier diffusion is about the same value as the film thickness, so that surface phenomena govern the recombination process in all phases of photoconductivity.

[Ref. 7700]



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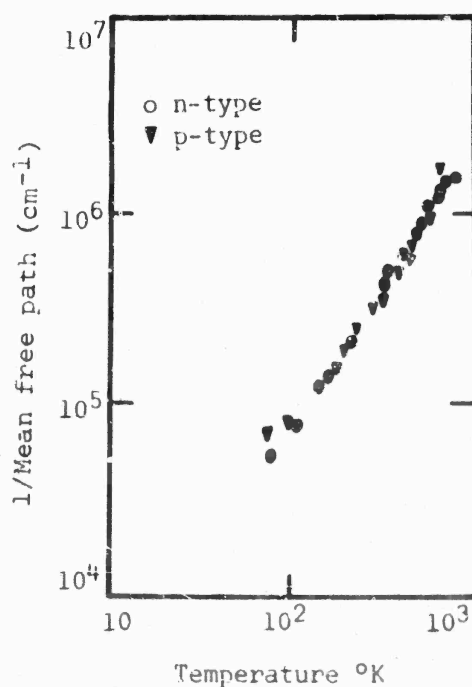
LEAD SULFIDE

CARRIER DIFFUSION

Mean Free Path

Symbol	Sample	Test Measurement	Temperature °K	Ref.
$L_n^*$	$\sim 10^{-6}$ cm	calculated from mobility data	300	4602

\*The electron mean free path ( $L_n$ ) is calculated from  $3\mu/4e(2\pi mkT)^{1/2}$ . This formula, is essentially, with a factor of 1.8, identical to  $L=(D\tau)^{1/2}$ .

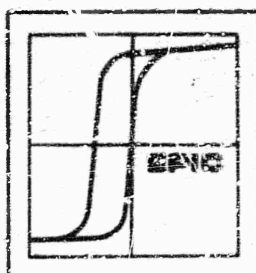


Reciprocal mean free path as a function of temperature for single crystal n- or p-type lead sulfide from 77-600°K.  
Calculated from Hall mobility data.

Symbol	Sample	$n, 10^{17} \text{ cm}^{-3}$
o	n-type	3.6
▼	p-type	0.88

[Ref. 288]

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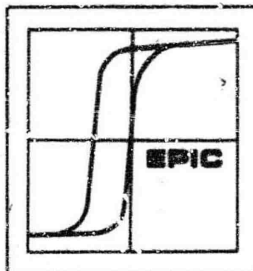
# LEAD SULFIDE

## CROSS SECTION

<u>Symbol</u>	<u>Value (cm<sup>2</sup>)</u>	<u>Sample</u>	<u>Temperature</u>	<u>Ref.</u>
$\sigma_n$	$10^{-17}$	Synthetic single crystal, n-type $n = 7.1 \times 10^{17} \text{ cm}^{-3}$ .	PME & PC measured at 77°K	7170
$\sigma_p$	$10^{-21}$	Films, $8 \times 10^{-4} \text{ cm}$ thick $n = 12 \times 10^{15} \text{ cm}^{-3}$ , .24 $\Omega$ resistivity	PC at 300-320°K	3580
$\sigma$	$1.3 \times 10^{-19}$	Effective cross section calculated from recombination radiation and optical data.	77-522°K	14453

PME is Photomagnetoelectric effect

PC is Photoconductivity



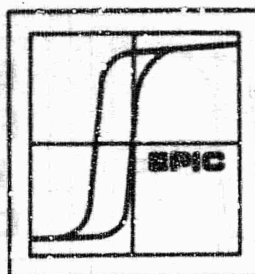
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DEBYE TEMPERATURE  $\theta_D$

<u><math>\theta_D</math></u>	<u><math>^{\circ}\text{K}</math></u>	<u>Sample</u>	<u>Ref.</u>
149	20	Calculated from molar heat in synthetic single crystal lead sulfide, $\sigma_{290^{\circ}\text{K}} \sim 150 (\Omega \text{ cm})^{-1}$ .	6001
159	25		
167	30		
176	35		
184	40		
190	45		
197	50		
202	55		
207	60		
210	65		
214	70		
217	75		
218	80		
219	85		
220	90		
222	95		
223	100		
223	105		
225	110		
225	115		
227	120		
230	130		
227	140		
227	150		
226	160		
226	170		
227	180		
228	190		
227	200		





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# LEAD SULFIDE

## DIELECTRIC CONSTANT

$\epsilon_{\infty}$ (1)	$\epsilon_{\infty}$ (2)	$\lambda_0$ ( $\mu$ )	Sample	Temp. °K	Ref.
16.5	15.8	0.68	Calculated from the refractive index for single crystal epitaxial films at $\lambda = 2.0-15.0 \mu$	373	22079
17.4	16.9	0.77		300	
19.2	17.6	1.47		77	

(1)  $n^2 \sim \lambda^2$  extrapolated to  $\lambda^2 = 0 \mu$ ,  $n_0^2 = \epsilon_{\infty}$

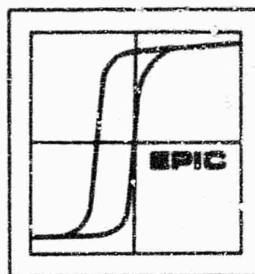
(2)  $(n^2-1)^{-1} \sim \lambda^{-2}$ , evaluated at 3 temperatures

Symbol	Value	Sample	Temp. °K	Ref.
$\epsilon_{\infty}$	17.2	Single crystal epitaxial film, 0.2-8 $\mu$ thick calculated from $n^2 \sim \lambda^2$ for $\lambda = 0.2-8.0 \mu$	300	17195
$\epsilon_{\infty}$	16.8	Single crystal n-type epitaxial films ( $n^2 \sim \lambda^2$ )	300	13718

$\epsilon_{\infty}$  = optical (high frequency) dielectric constant

$\epsilon_0$  = static dielectric constant

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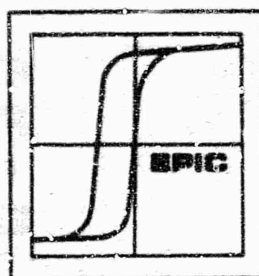
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DIELECTRIC CONSTANT

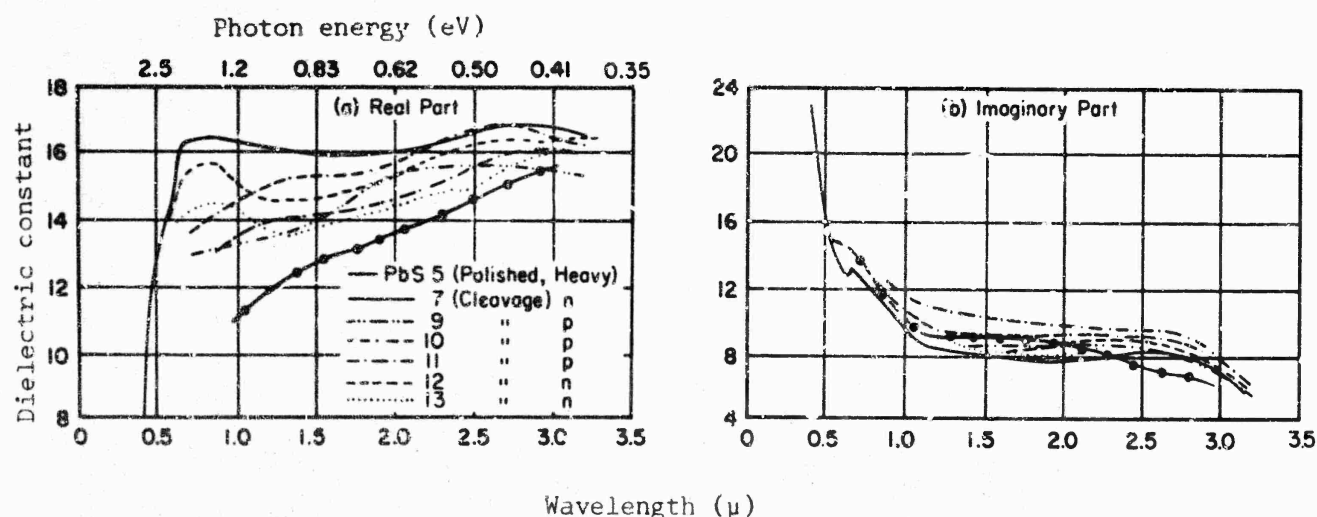
<u>Symbol</u>	<u>Value</u>	<u>Sample</u>	<u>Test Measurement</u>	<u>Temp. (°K)</u>	<u>Ref.</u>
$\epsilon_0$	161.5±0.6	natural single crystal galena, $\rho \sim 5 \Omega \text{cm}$	microwave at 25 Gc		26152
$\epsilon_\infty$	17.3	epitaxial films 180-500 Å thick	IR transmission at 77°K and 300°K	300	24929
$\epsilon_0$	174.4	$n = 5 \times 10^{18}, 10^{19} \text{cm}^{-3}$	"	"	"
$\epsilon_0$	140±20	natural single crystals $n = 10^{16} \text{cm}^{-3}$	IR transmission and reflection		26151



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# LEAD SULFIDE

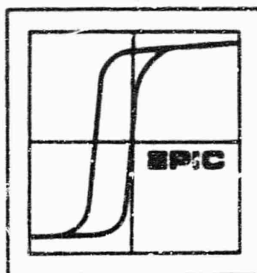
## DIELECTRIC CONSTANT ( $\epsilon$ )



In (a), the real part of the dielectric constant, calculated from  $n(1-k^2)$  is plotted as a function of the wavelength. In (b), the imaginary part of the dielectric constant calculated from  $2n^2k$  is plotted as a function of the wavelength. The samples are a series of natural and synthetic single lead sulfide crystal, (100) oriented.

Sample no.	Type	Material	$n$ ( $10^{17} \text{ cm}^{-3}$ )
5	p-	natural	600
7	n-	"	4.5
9	p-	synthetic	200
10	p	natural	13
11	p	synthetic	15
12	n	natural	70
15	n	"	0.6

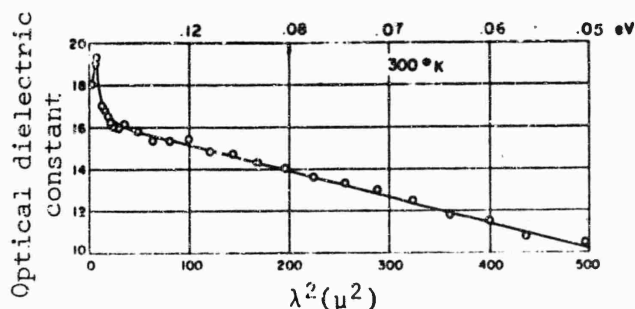
[Ref. 3453]



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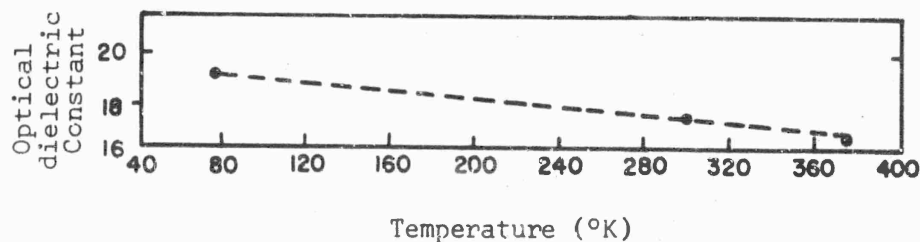
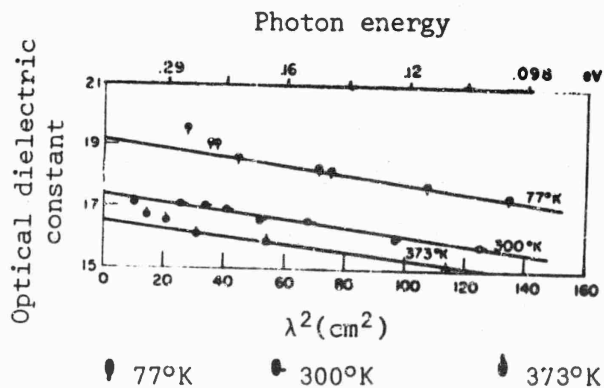
## DIELECTRIC CONSTANT



The refractive index squared as a function of the wavelength squared for single crystal lead sulfide. The peak at  $\lambda^2 \approx 8\mu^2$ , ( $2.8\mu$ ), is the result of the increase in the extinction coefficient at the absorption edge. [Ref. 13718]

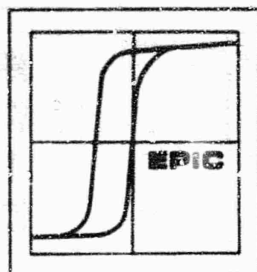
Optical or high frequency dielectric constant, ( $\epsilon_\infty = n^2$ ),  $\sim$  wavelength squared for single crystal lead sulfide epitaxial films, at 3 temperatures. These curves describe the contribution of the free carriers and lattice vibrational modes to the dispersion and are reliable at this wavelength region well below the absorption edge.

[Ref. 22079]



Optical dielectric constant as a function of temperature for single crystal epitaxial lead sulfide films.

[Ref. 22079]



LEAD SULFIDE

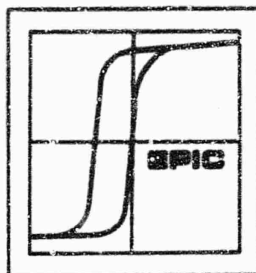
EFFECTIVE MASS ( $m^*$ )

Symbol	Value ( $m_0$ )	Sample Single Crystal	Test Measurement	Temp. ( $^{\circ}$ K)	Ref.
$m_n$	0.22	n-, p-type	Hall and resistivity to 600 $^{\circ}$ K	77-200	288
$m_p$	0.10 (good only up to 0 $_D$ (194 $^{\circ}$ K))	$n=10^{15}-10^{19}$ cm $^{-3}$	"	"	
$m_n$	0.22	pure, natural lead sulfide $n=3.5 \times 10^{15}$ cm $^{-3}$	electrical	100	19724
$m_n$	0.66	"	"	300	"
$m_n=m_p$	0.25	n-, p-type $n \sim 10^{16}$ cm $^{-3}$	thermal emf	300	3679
$m_n$	0.12 $\pm$ 0.01	natural (galena) n-type, (100) plane $n=7.5 \times 10^{18}$ cm $^{-3}$	optical reflectivity and Faraday rotation (magneto-optical)	77	14838
$m_n$	0.14 $\pm$ 0.04	n-type, (100) plane $n=3 \times 10^{18}$ cm $^{-3}$	magnetic susceptibility to 125 kG	4	19043
$m_n$	0.176 $\pm$ 0.012	natural (galena) n-type, $n \sim 2 \times 10^{19}$ cm $^{-3}$	Faraday rotation $\lambda = 3-5 \mu$	300	22573
$m_n=m_p$	0.17	n, p-type	Hall	150	11386
$m_n=m_p$	0.50 $\pm$ 0.20	"	thermal emf	800-1200	"
$m_c^{**}$	0.118 $\pm$ 0.01	(100) plane n-, p-type	magneto-optical	77	16127
$m_v^{**}$	0.115 $\pm$ 0.01	epitaxial films	"		
$m^{\dagger}$	0.055 $\pm$ 0.003	natural crystal (unstrained)	Faraday rotation		
$m^{\dagger}$	0.0515 $\pm$ 0.002	epitaxial films	"		

\*\*  $m_c$  is conduction band effective mass,  $m_v$  is valence band effective mass

$\dagger$  reduced effective mass





LEAD SULFIDE

EFFECTIVE MASS ( $m^*$ )

<u>Symbol</u>	<u><math>m_t</math></u>	<u><math>m_l</math></u>	<u>Method</u>	<u>Temperature</u>	<u>Ref.</u>
$m_c$	.080 $\pm$ .01	.105 $\pm$ .015	Shubnikov-de Haas Measurements	4°K	24930
$m_v$	.075 $\pm$ .01	.105 $\pm$ .015	"	"	"

In both bands the constant energy surfaces are prolate ellipsoids of revolution located at the L point. Mass anisotropies show a weak dependence on carrier concentration which, for the two samples of p-type lead sulfide was 3.2 and  $2.5 \times 10^{18} \text{ cm}^{-3}$ .

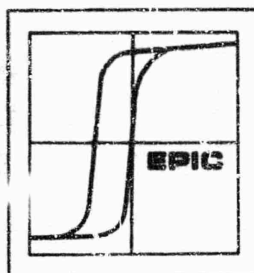
$m_t$  is Transverse Cyclotron Mass

$m_l$  is Longitudinal Cyclotron Mass

$m_n$  is electron effective mass

$m_p$  is hole effective mass

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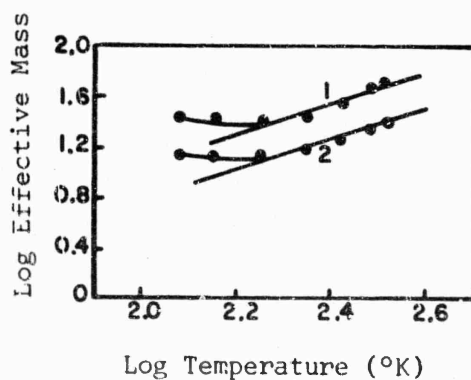


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EFFECTIVE MASS

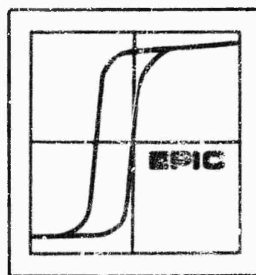


Log effective mass as a function of log temperature calculated for two scattering coefficients. 1)  $r = 0$  and 2)  $r = 1$ . The samples are natural single crystals and  $n$  varies from  $10^{16}$  to  $10^{18} \text{ cm}^{-3}$ .

$m_n^* = 0.22 m_0$  at  $300^\circ\text{K}$  is calculated on the basis of  $r = 1$ , which latter, from mobility values, is apparently more probable than  $r = 0$ .

[Ref. 22574]

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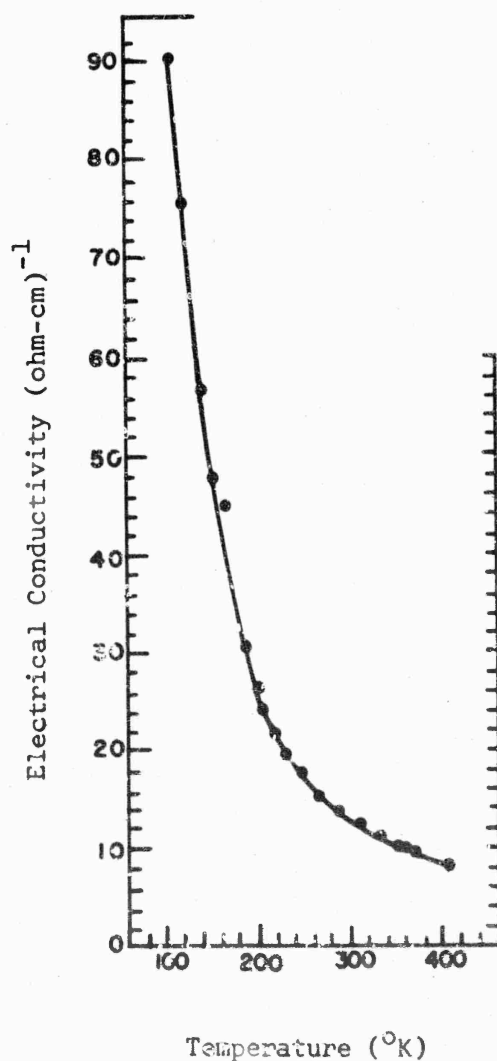


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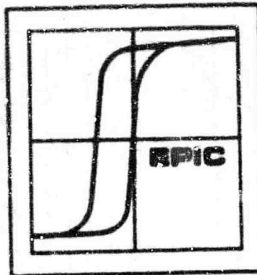
LEAD SULFIDE

ELECTRICAL CONDUCTIVITY



Electrical conductivity as a function of temperature in natural single crystals of lead sulfide. Crystals were homogeneous with traces of cadmium and silver.

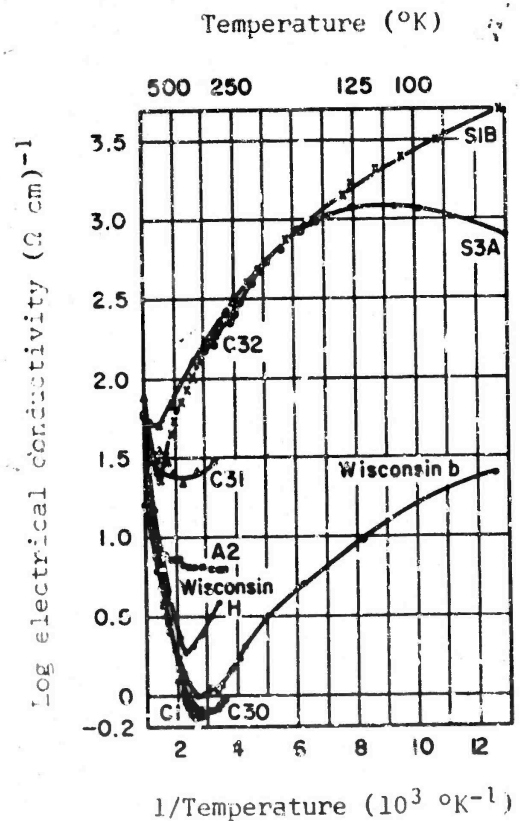
[Ref. 22574]



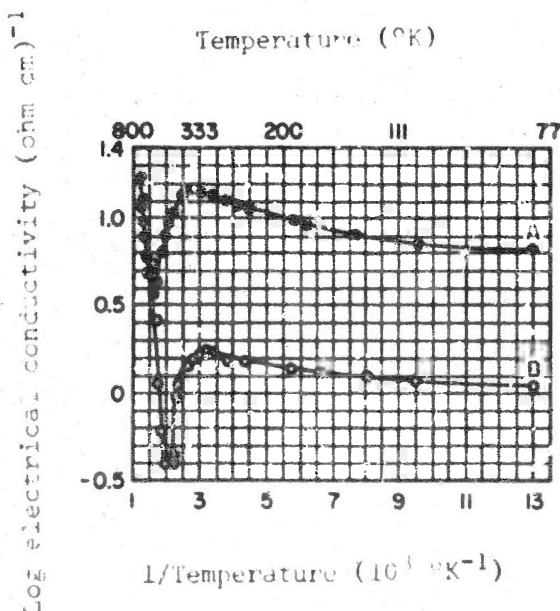
# LEAD SULFIDE

## ELECTRICAL CONDUCTIVITY

Log electrical conductivity as a function of reciprocal temperature for single crystal lead sulfide cleaved on (100). Carrier concentration values from  $10^{16}$  to  $10^{18}$  cm in these natural galena samples, but more definite sample data are not available.

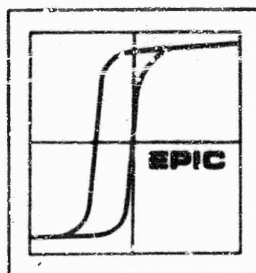


[Ref. 2833]



Log electrical conductivity as a function of reciprocal temperature for compressed powder samples of lead sulfide, sintered at 1100°K for several hours in an  $H_2S$  atmosphere. Block density is about 80% of a single crystal. 2 p-type samples. (See page 51 for further discussion)

[Ref. 3904]



# LEAD SULFIDE

## ELECTRICAL CONDUCTIVITY

Electrical conductance as a function of reciprocal temperature for p-type lead sulfide films prepared and maintained in a nitrogen atmosphere.

$n, 10^{16} \text{ cm}^{-3}$

- $\Delta$  7.4
- $\times$  7.4
- $\bullet$  3.7
- $\blacktriangle$  1.3
- $\nabla$  5.4
- $\blacktriangledown$  4.0
- $\circ$  4.0

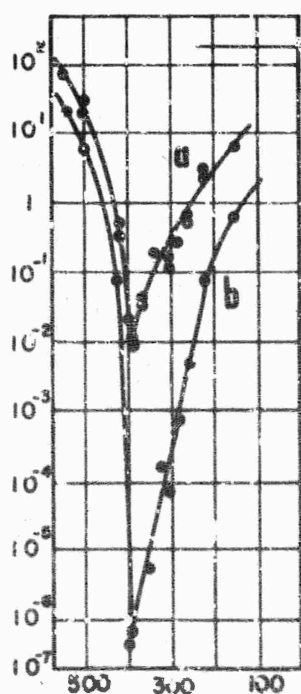
[Ref. 3580]

Temperature ( $^{\circ}\text{K}$ )

Electrical conductance ( $10^{-6} \text{ ohms}$ )



Electrical conductivity ( $\Omega \text{ cm}^{-1}$ )



increasing sulfide content

$1/\text{Temperature} (10^2 \text{ }^{\circ}\text{K}^{-1})$

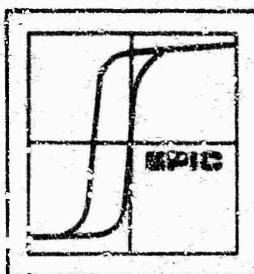
Electrical conductivity as a function of annealing temperature for a 1.4 microns lead sulfide film. The film had originally an excess of sulfur and was annealed at  $T_v$  to remove varying amounts of sulfur. Conductivity was then measured for curve,

- a) at 20  $^{\circ}\text{C}$
- b) at -203  $^{\circ}\text{C}$  (liquid air)

( $T_v$ ) Temperature  $^{\circ}\text{C}$

[Ref. 5844]





# LEAD SULFIDE

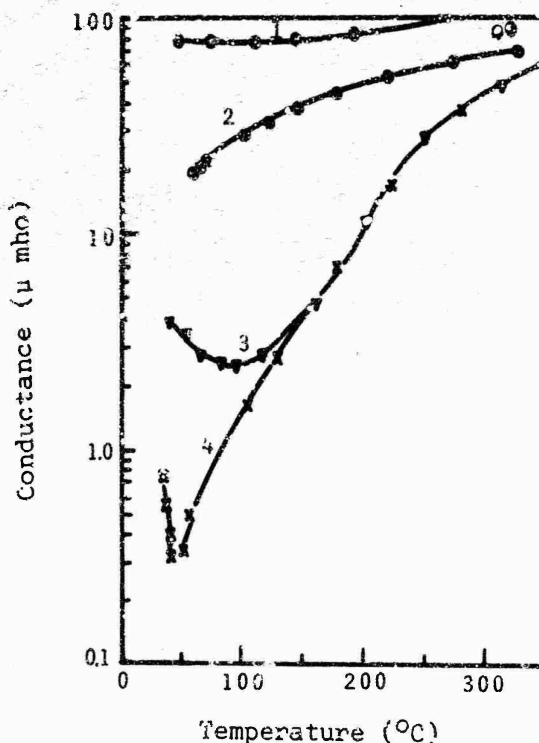
## ELECTRICAL CONDUCTIVITY

Electrical conductance as a function of temperature for various oxygen pressures for a vacuum evaporated n-type lead sulfide film, 0.026 microns thick. Carrier concentration  $10^{17} \text{ cm}^{-3}$ .

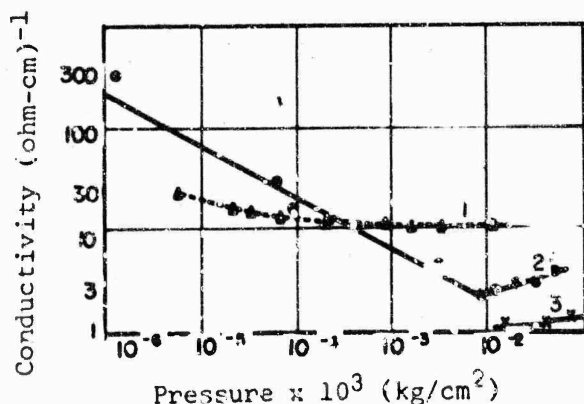
### mm oxygen pressure

1.  $6 \times 10^{-6}$
2.  $2 \times 10^{-4}$
3.  $1 \times 10^{-3}$
4.  $2 \times 10^{-3}$

These curves are reproducible.



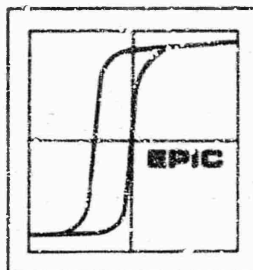
[Ref. 2789]



Electrical conductivity as a function of oxygen pressure for vacuum evaporated n-type lead sulfide films as a function of pressure. Films 0.7 microns thick.

	$T^{\circ}\text{C}$	$n, 10^{17} \text{ cm}^{-3}$
1.	310	5.7
2.	155	40.0
3.	200	1.7

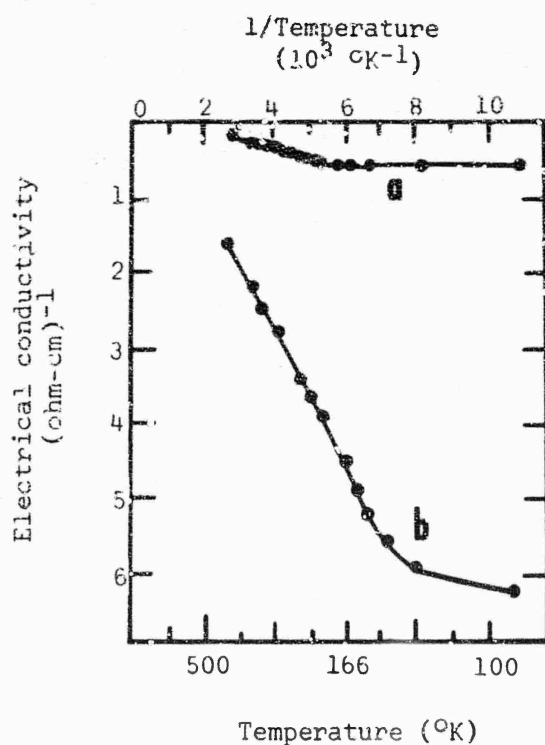
[Ref. 2789]



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LEAD SULFIDE

ELECTRICAL CONDUCTIVITY

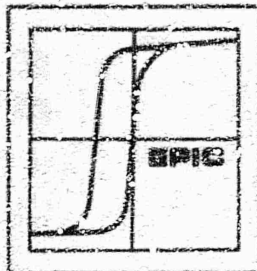


Log electrical conductivity as a function of reciprocal temperature for vacuum deposited lead sulfide films at:

- a) 10 Cc
- b) dc

[Ref. 639]

Microwave conductivity of layers depends much less on temperature than does dc conductivity. Apparently these films are inhomogeneous layers of crystallites separated by regions of low conductivity.



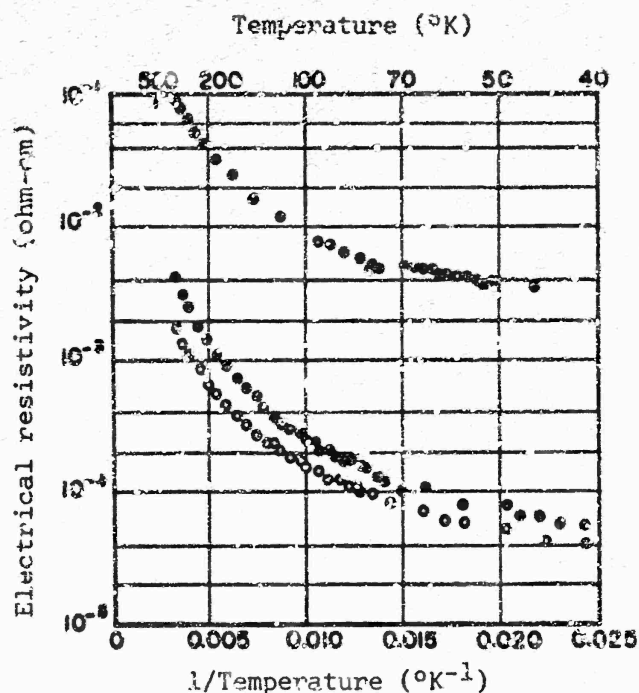
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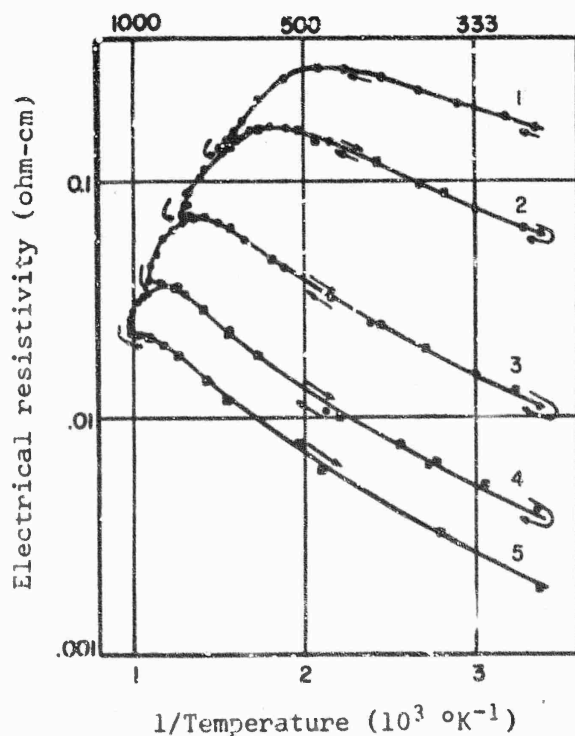
### ELECTRICAL RESISTIVITY

Electrical resistivity as a function of reciprocal temperature for single crystal lead sulfide.

Symbol	Sample	$n, 10^{18} \text{ cm}^{-3}$
*	n-type, natural	0.2
•	n-type, synthetic	7
o	p-type, synthetic	3



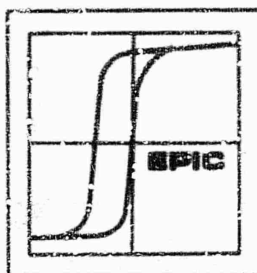
[Ref. 776]



Electrical resistivity as a function of reciprocal temperature for natural single crystal n-type lead sulfide, in an argon atmosphere. Curve 1 - 700°K maximum, and curve 2 - 800°K maximum begin to show changes in composition. Curve 3 at 919°K maximum shows more change. Curve 4 is held at 1023°K for an hour. Curve 5 is the cooling curve for 4 and the sample shows an apparently infinite slope to its resistivity curve.

- heating curve
- cooling curve

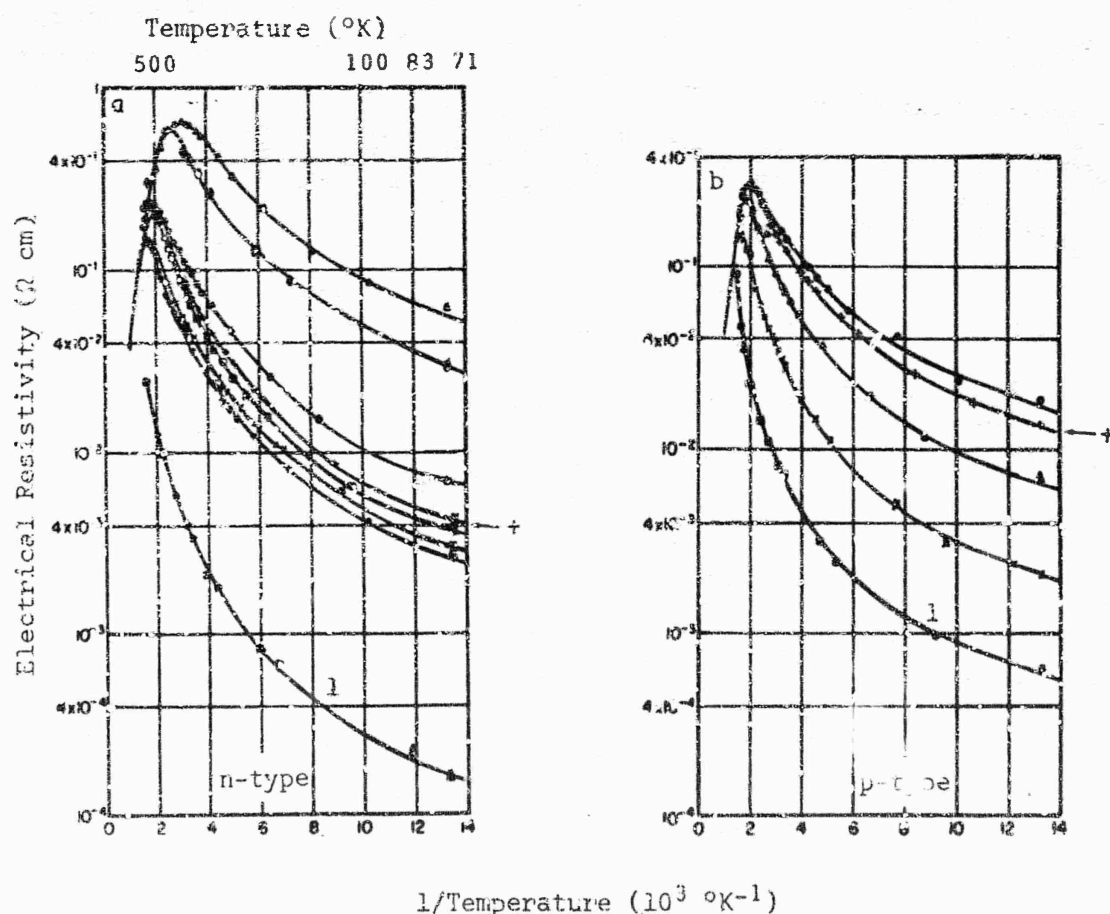
[Ref. 2137]



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# LEAD SULFIDE

## ELECTRICAL RESISTIVITY



Electrical resistivity as a function of reciprocal temperature for natural single crystals of lead sulfide.

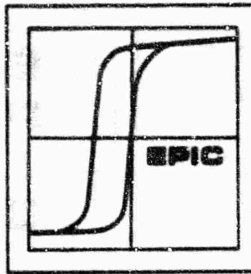
The natural n-type crystals were held at 500°C in sulfur vapor for 20 hours at various pressures from  $3.10^{-5}$  to 0.3 mm Hg and then quenched to 20°C. The resultant n-type (excess lead) samples are shown in (a) and the p-type (excess sulfur) samples are shown in (b). Carrier concentrations are shown on page 53.

The treatment is reversible; the crystals may be changed from n- to p-type and back again. Measurements are reproducible.

- 1 This curve on both graphs represents data taken on untreated synthetic crystals, prepared as n- and p-type samples.
- + "Natural" This curve on both graphs indicates the untreated natural n-type lead sulfide crystals used in the experiment.

[Ref. 3612]





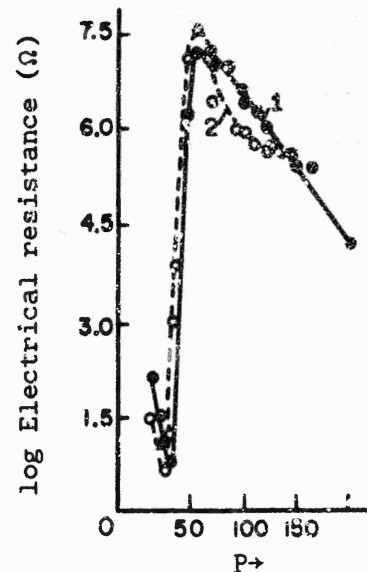
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# LEAD SULFIDE

## ELECTRICAL RESISTIVITY

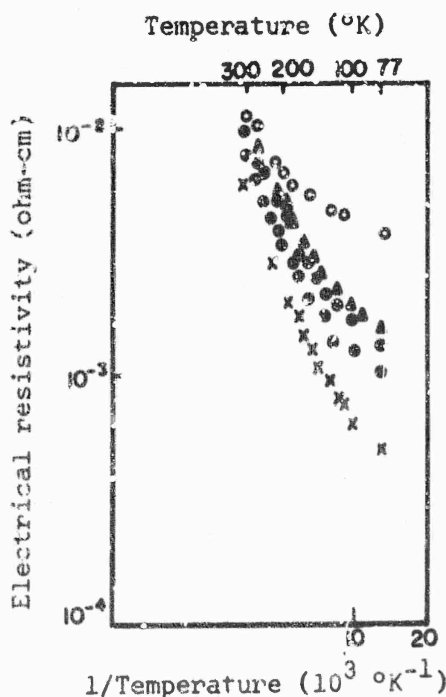
Log electrical resistance as a function of pressure in single crystal lead sulfide.

Symbol	Sample	$n, 10^{18} \text{ cm}^{-3}$
1	n-type	4.9
2	p-type	1.5



Pressure ( $10^3 \text{ kg/cm}^2$ )

[Ref. 16135]



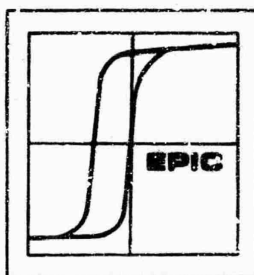
Electrical resistivity as a function of reciprocal temperature in single crystal n-type epitaxial lead sulfide films.

Symbol	$n = 2 \times 10^{18} \text{ cm}^{-3}$
○, x	1.26μ thickness
•	4.69μ thickness

The other samples are in this range.

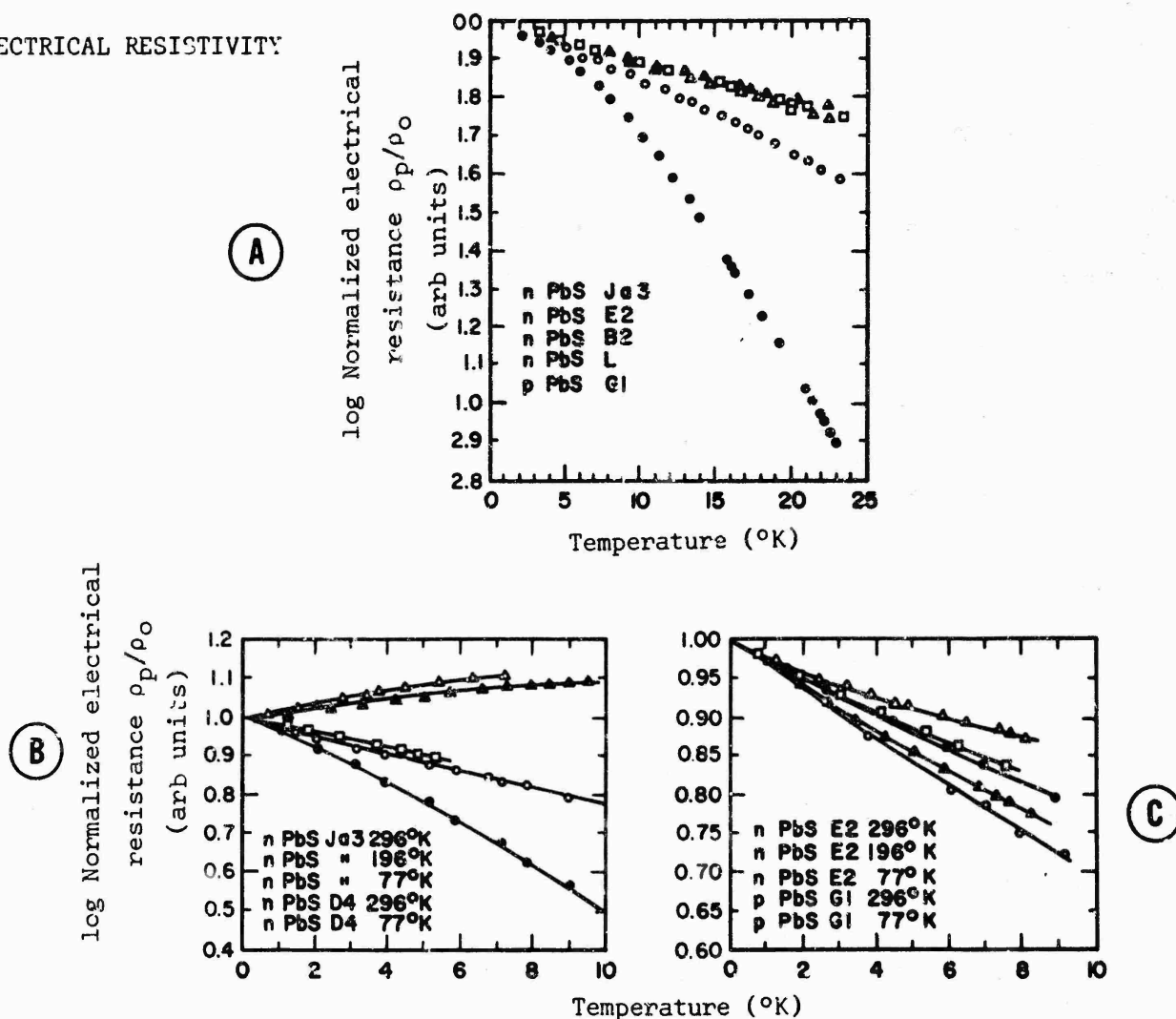
[Ref. 22079]





LEAD SULFIDE

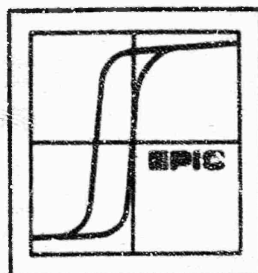
ELECTRICAL RESISTIVITY



Normalized electrical resistance as a function of pressure in n- and p-type single crystal lead sulfide at several temperatures. Data points were taken at increasing and decreasing pressure.

- (A) Ja3 is near intrinsic, n-type, the other samples are extrinsic and either n-, or p-type. Measurements are at 296°K.
- (B) Ja3 is measured here at 296, 196 and 77°K for comparison with an impure n-type sample at 296 and 77°K.
- (C) n-, and p-type extrinsic samples are measured at 3 temperatures.

[Ref. 14839]



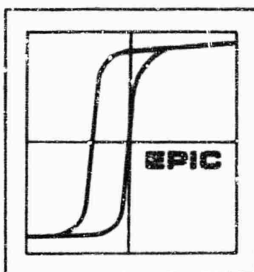
**LEAD SULFIDE**

**ELECTROACOUSTIC PROPERTIES**

<u>Symbol</u>	<u>Value</u>	<u>Sample</u>	<u>Test Measurement</u>	<u>Temp. (°K)</u>	<u>Ref.</u>
LO	26.3±0.4 meV	single crystal p-type	calculated from current-voltage curves	4.2	2506
TO	27.3 meV	natural single crystal galena $\rho=5\Omega\text{cm}$	microwave measurement at 25 Gc	300	26152
TO	8.27 meV	single crystal epitaxial film	IR transmission at 77°K and 300°K		24929
LO	26.4 meV	on halite			"
TO	8.68 meV	film	transmission	300	26151
LO	26.3 meV	natural single crystal $n=10^{16}\text{cm}^{-3}$	reflectivity 40-2000 $\mu$	300	"

TO is the transverse optical phonon branch

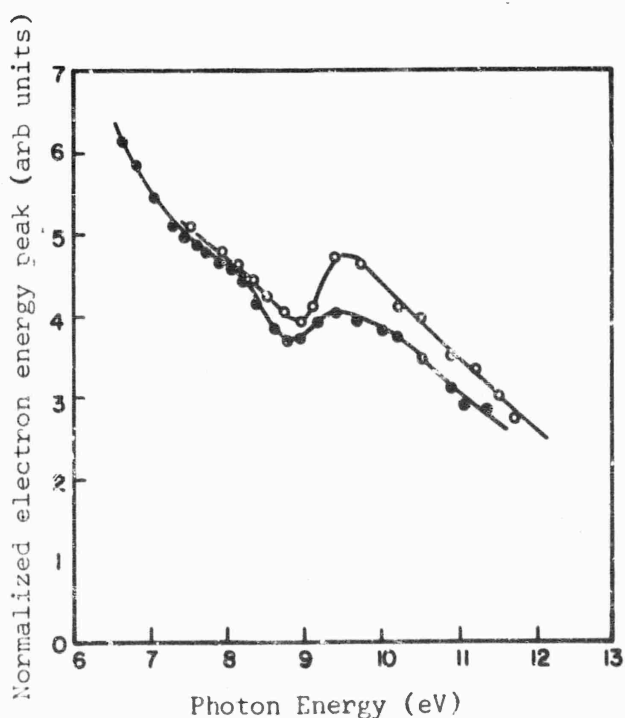
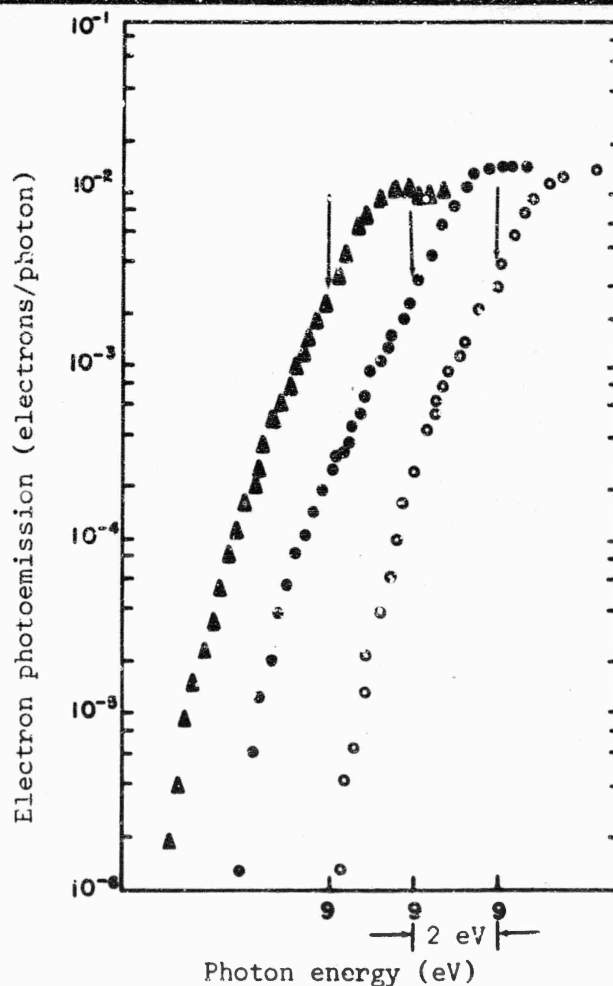
LO is the longitudinal optical phonon branch



# LEAD SULFIDE

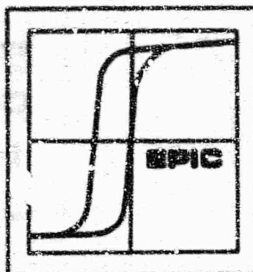
## ELECTRON PHOTOEMISSION

Photoelectric yield of three samples showing inflection point near 9 eV. Around 9 eV the distribution become higher and narrower indicating an increase in the low energy electrons. Above 9 eV the distribution indicates a decrease in low energy electrons.



Peak height of electron energy distribution as a function of photon energy in two natural lead sulfide (galena) single crystal samples at 300°K.

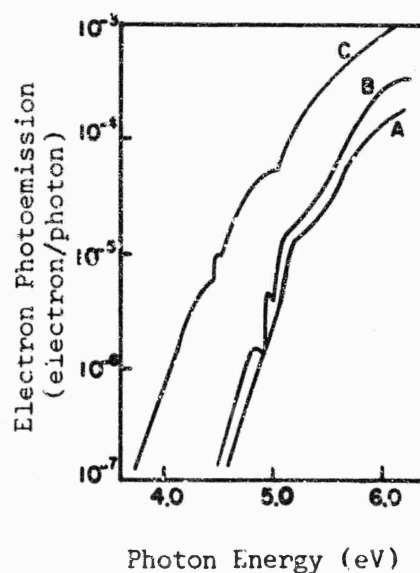
[Ref. 13554]



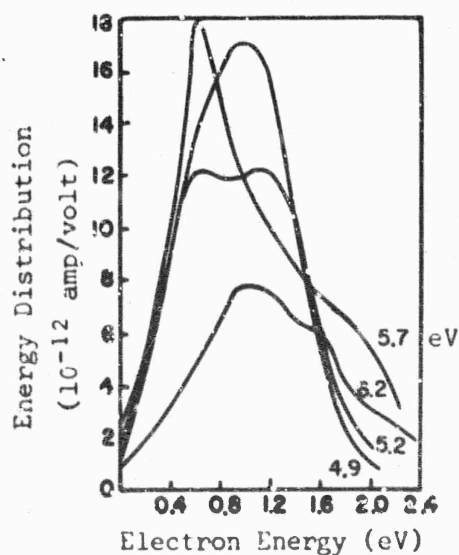
## LEAD SULFIDE

### ELECTRON PHOTOEMISSION

Photoelectric yield curves for single crystal natural galena (100) cleavage plane. Cleavage and annealing are carried out in an argon atmosphere. A) an untreated surface. B) a cleaved surface, and C) a cleaved and annealed or ion-bombarded and annealed surface. The photothreshold is  $3.8 \pm 1$  eV.



[Ref. 22709]

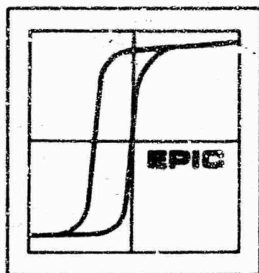


Energy distribution of electrons emitted at various photon energies in natural single crystal lead sulfide employing (100) cleavage plane, ion-bombarded.

A high density of states in the conduction band would be indicated by peaks or shoulders in the energies of the emitted electrons, independently of the photon energy. In the 2 eV range of the threshold, there are no clear indications of these high density of states regions.

[Ref. 22709]

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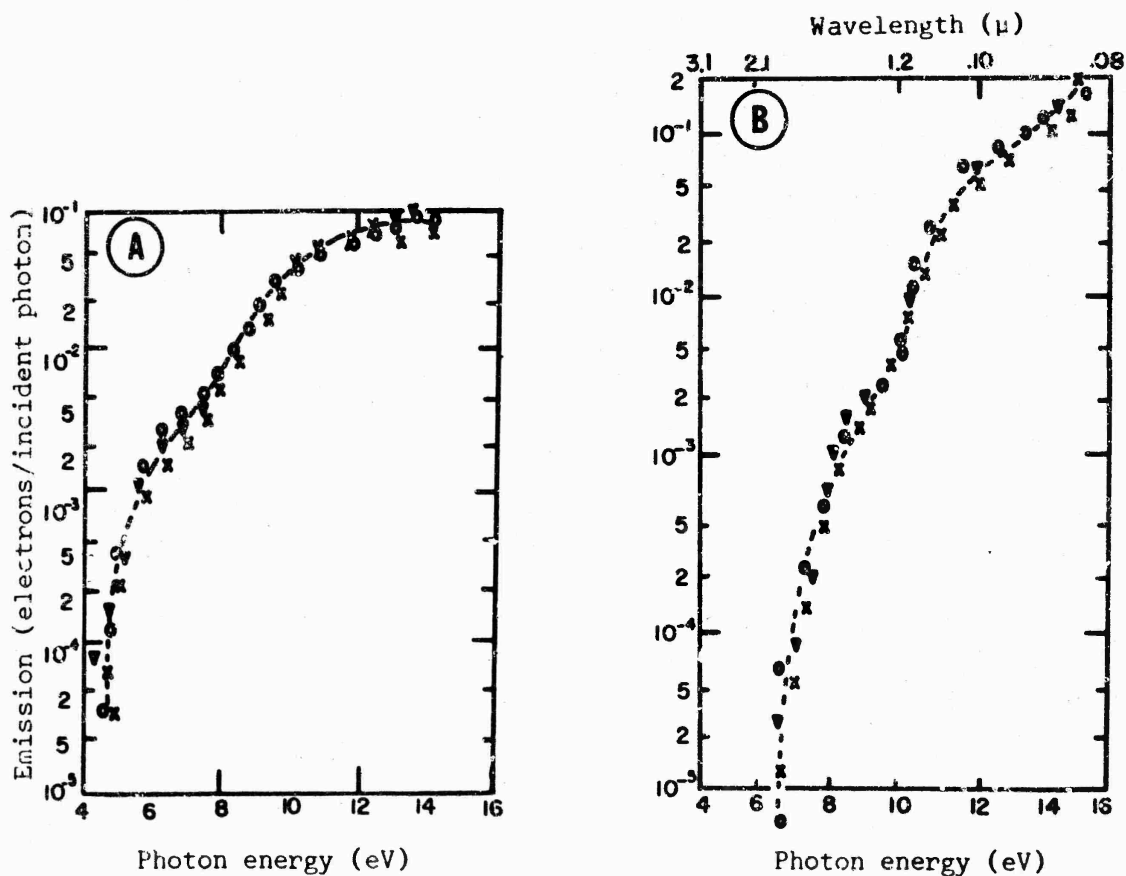


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ELECTRON PHOTOEMISSION



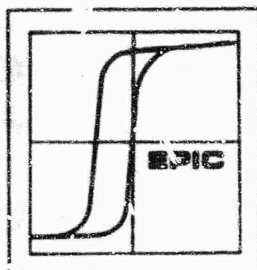
External photoelectric yields as a function of photon energy at 300°K.

- A. 3 natural single crystal lead sulfide samples measured on (100) surface cleaved in vacuum.
- B. Polycrystalline, chemically deposited films.

[Ref. 16824]



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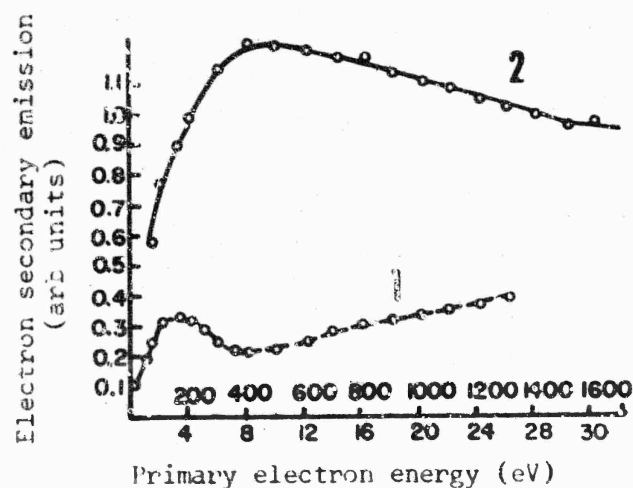


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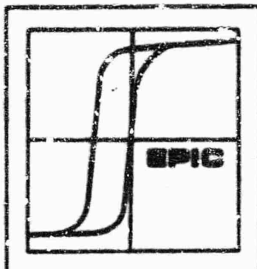
ELECTRON SECONDARY EMISSION ( $\sigma$ )



Secondary electron emission coefficient  $\sigma$ , as a function of the primary electron energy for single crystal lead sulfide.

- 1) at low primary electron energy (0.5-30 eV)
- 2) at intermediate electron energy (50-1500 eV)

[Ref. 21307]



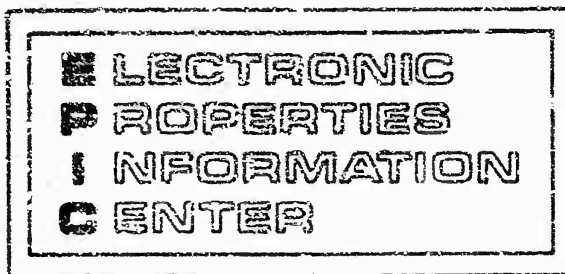
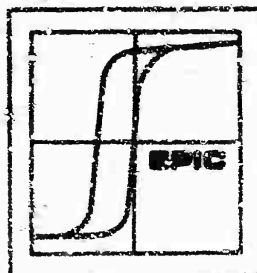
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LEAD SULFIDE

ENERGY BANDS

Symbol	Value	Sample	Measurement Method	Temp.	Ref.
$\Delta E_g/\Delta T$	$3.7 \times 10^{-4} \text{ eV/}^\circ\text{K}$	single crystal (galena)	optical absorption $\lambda = 1-10 \mu$	90-400°K	533
$\Delta E_g/\Delta T$	$4 \times 10^{-4} \text{ eV/}^\circ\text{K}$	single crystal natural & synthetic n&p-type	optical absorption $\lambda = .5-3 \mu$	293-520°K	3452
$\Delta E_g/\Delta T$	$4.0 \times 10^{-4} \text{ eV/}^\circ\text{K}$	single crystal n-type	optical absorption $\lambda = 2.5-10 \mu$	20-400°K	3768
$\Delta E_g/\Delta T$	$5 \times 10^{-4} \text{ eV/}^\circ\text{K}$	(dilatational gap change)	magneto-optical	77-300°K	14838
$\Delta E_g/\Delta P$	$-6.9 \times 10^{-6} \text{ eV/cm}^2/\text{kg}$ (corrected for mass variation)	single crystal n-type, nearly intrinsic	electrical conductivity at pressures to 30,000 kg/cm <sup>2</sup>	300°K	14839
	$-7.9 \times 10^{-6} \text{ eV/cm}^2/\text{kg}$ (calculated for $\mu_n = \mu_p$ )	n-type $3 \times 10^{15} \text{ cm}^{-3}$	"		
	$-8 \times 10^{-6} \text{ eV/cm}^2/\text{kg}$	single crystal	optical absorption		
$\Delta E_1/\Delta T,$ $\Delta E_2/\Delta T,$ $\Delta E_3/\Delta T$	$\approx 10^{-4} \text{ eV/}^\circ\text{K}$	From data taken on single crystal and thin film lead sulfide; infra- red reflectivity and transmission measurements. (See page 47 )		77-300°K	14189

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# LEAD SULFIDE

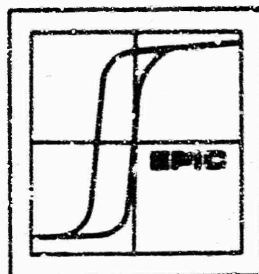
## ENERGY BANDS

### Deformation Potential $\Xi$

<u>Value</u>	<u>Sample</u>	<u>Method</u>	<u>Temp.</u>	<u>Ref.</u>
4.3±0.6eV*	single crystal bulk and epitaxial films	magneto-optical	77°K	16127
3.45 eV		optical absorption	300°K	14839
6.9±0.4eV	Natural galena single crystal, n-type $n = 10^{16}$ and $10^{17}\text{cm}^{-3}$ (100) and (110) oriented	Piezoelectric resis- tance measurements from 4-300°K	90°K	25751
5.01 eV	Calculated for conductivity band			26153
3.25 eV	Calculated for valence band			26153

The Augmented Plane Wave method was used to calculate the energy band structure of lead sulfide and then the deformation potential values for conductivity and valence bands.

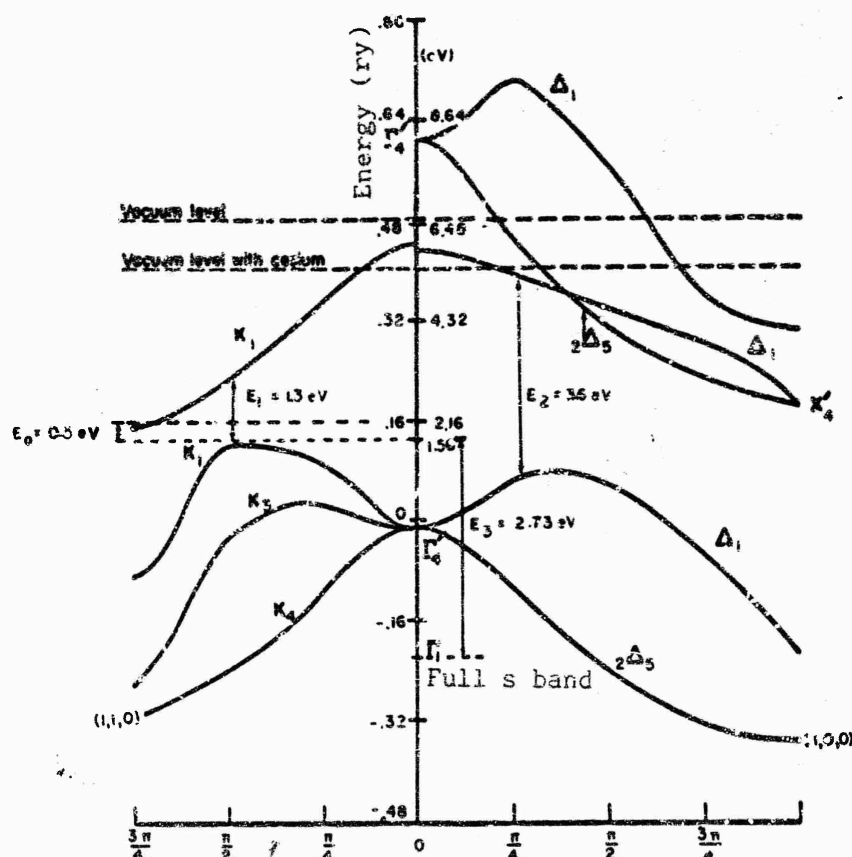
\*Effective deformation potential for dilation.



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# LEAD SULFIDE

## ENERGY BANDS



Lead sulfide band structure (based on [Ref. 22572] and amplified by photoelectron emission data from lead sulfide and cesium coated lead sulfide samples.)

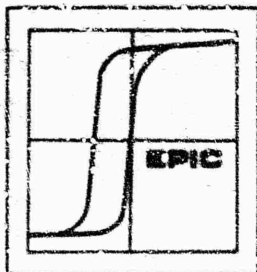
Measurements of photoelectric yield and electron energy distribution were made on natural lead sulfide crystals, (galena), in photocells at  $10^{-8}$  mm Hg pressure. Yield data for cesium coated samples and reflectivity values at 4-12 eV were used to amplify the available information used to compute the lead sulfide band structure.

In a semiconductor, if the energy gap is small and the electron affinity is large, an excited photoelectron, in order to escape must have an energy well above the threshold for scattering by valence band electrons and in consequence the photoelectric yield will be small. In the case of lead sulfide however, the photoelectric yield is large. In order to explain this, at  $k = 0$ , a band is identified as arising from the 6s electrons of lead, located at  $\sim 4.3$  eV below the top of the higher bands ( $k_1$  at 1.56 eV). The increased density of states in this assumed band is seen in the absorption data.

The  $\Delta_1 - \Delta_1$  transition given in (14189) as  $E_2$  at about 3.6 eV is also shown on the graph. This value is derived from reflectivity data.

[Ref. 13554]

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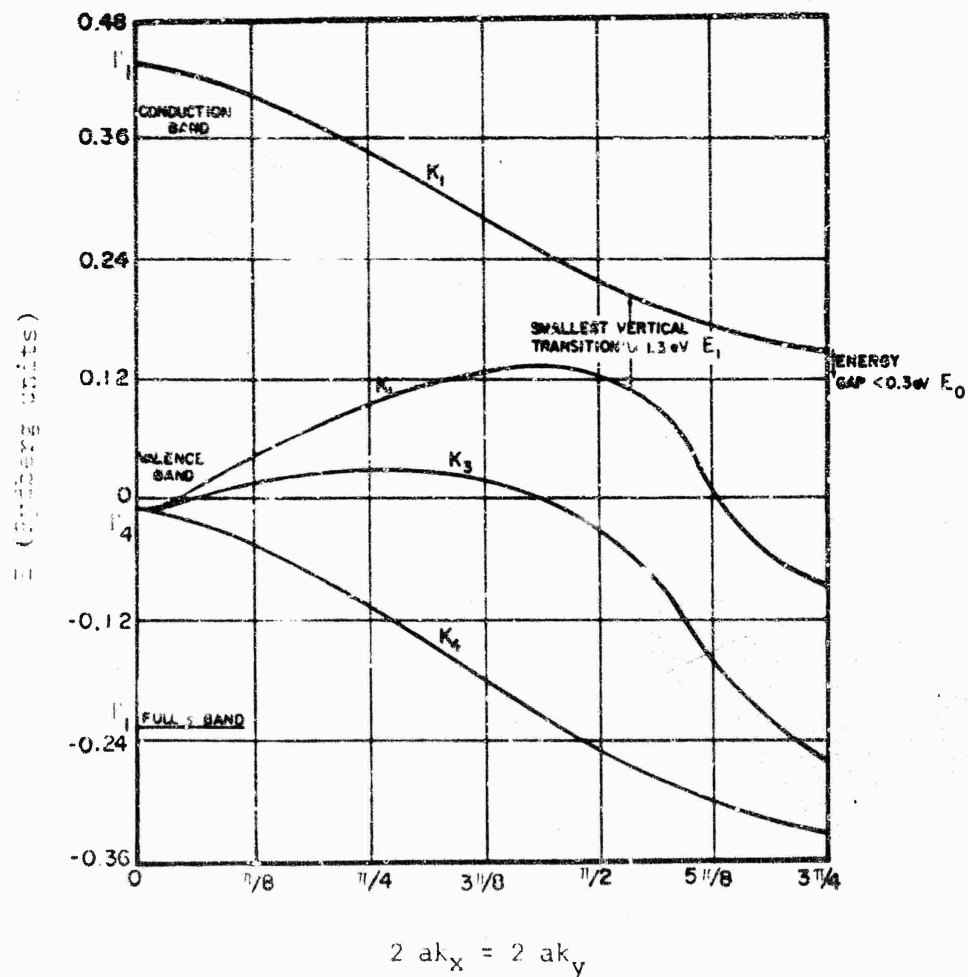


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ENERGY BANDS

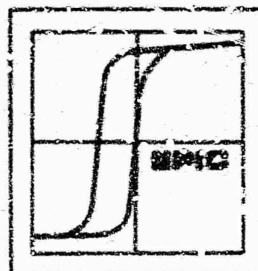


Valence band and conduction band of lead sulfide along the (1,1,0) direction.

1 Rydberg = 13.5 eV

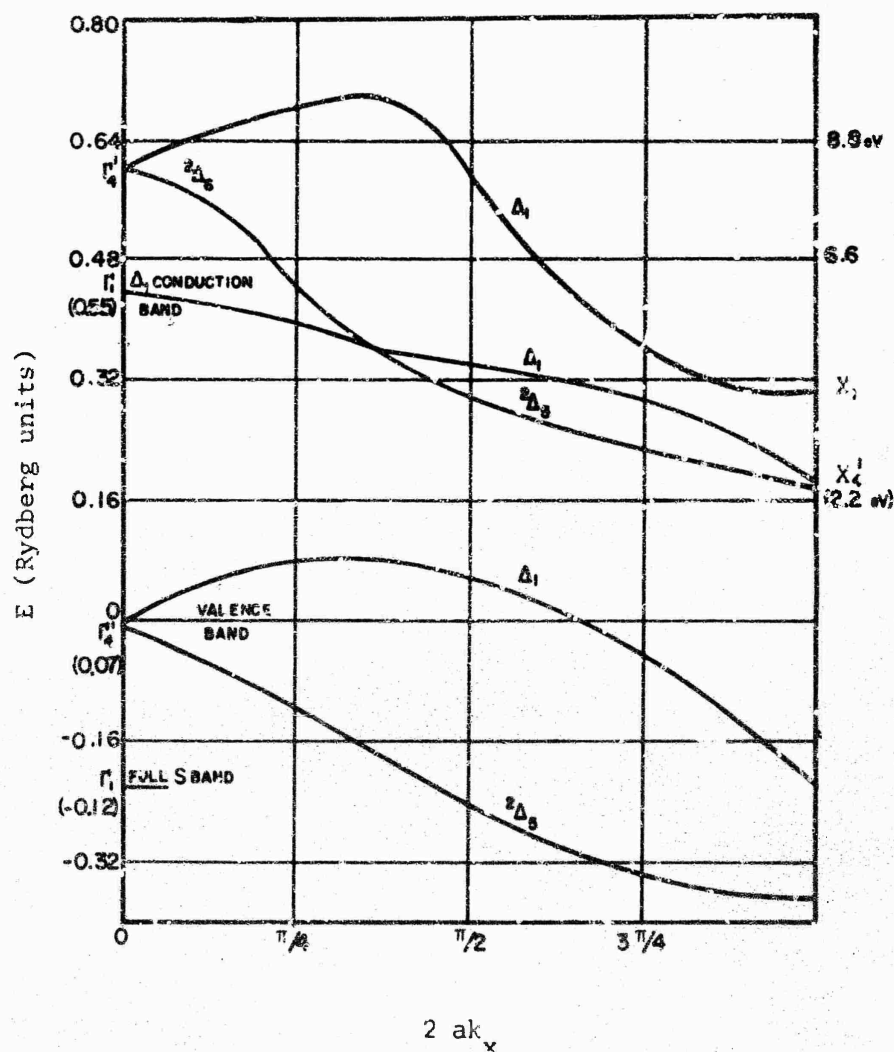
[Ref. 22572]





# LEAD SULFIDE

## ENERGY BANDS

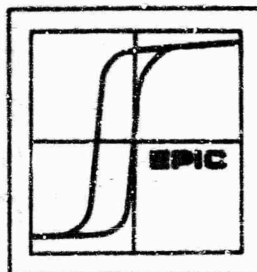


The valency band and the first two conduction bands of lead sulfide in the (1,0,0) direction. Full band width is approximately 6 eV. Conduction band width is approximately 7 eV. Lowest optical transition = 1.38 eV.

Splitting table giving full Cubic Harmonics in term. of sub-KH

$k=(a,0,0)$	$k=(1,0,0)$	$k=(a,a,0)$
$\Gamma_1$	$X_1$	$K_1$
$\Gamma_4$	$X_4^1 + X_5^1$	$K_1 + K_3 + K_4$
$\Gamma_5$		

[Ref. 22572]



## LEAD SULFIDE

### ENERGY BANDS

Band parameters of Lead Sulfide at 77°K, obtained by Faraday rotation measurements at 110 kOe.

$E_g$ (eV)	$m_{vc}$ [100]	$m_{vc}$ [110]	$g_v$	$g_c$	$n$	Sample
.309	.0545				6	n-, single crystal
.307	.0552				3.5	p-, free epitaxial
.278	.0515	.0508	-8.5	10.0	3.5	p-, film, (100)
.280	.0493		-3.8	5.3	1.1	n-, oriented.
.278	.0510				1.5	n-,
	$m_v^* = (0.115 \pm 0.01)m_0$				8.7	p-, synthetic single
	$m_c^* = (0.118 \pm 0.01)m_0$				.35	n-, natural single

The deformation potential  $Z_{vc} = 4.3 \pm 0.6$  eV and is calculated from  $E_g = 0.29$  eV

The effective g-factor for holes ( $g_v$ ) and electrons ( $g_c$ ) are approximately equal and opposite in sign

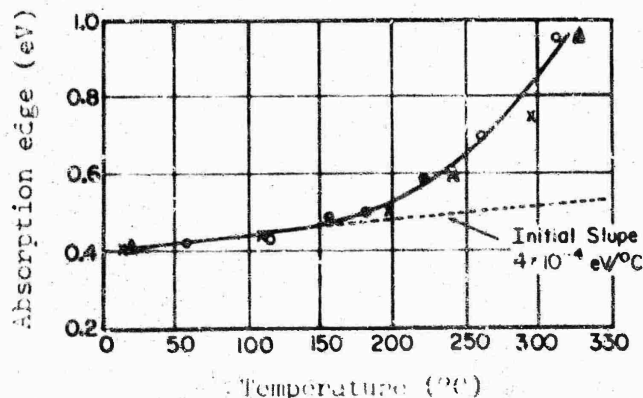
$m_{vc}^*$  is the reduced effective mass and is given for the plane as shown.

$m_v^*$  and  $m_c^*$  are valence and conduction band effective mass, respectively, and are given for samples 6 and 7

$n$  is carrier concentration, ( $10^{18} \text{ cm}^{-3}$ )

$E_g$  data has an experimental error of .002 to .005 eV

[Ref. 16127]

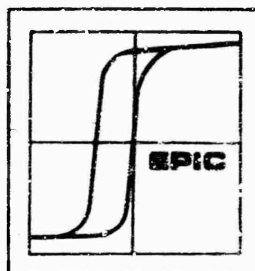


Absorption edge as a function of temperature for single crystal lead sulfide. The natural galena samples are all n-type, the synthetic material is p-type.  $\Delta E_g / \Delta T = 4 \times 10^{-4} \text{ eV/}^\circ\text{C}$ . Above 150°C, the crystal composition changes.

•, o, x = natural galena, n-type

Δ = synthetic galena, p-type

[Ref. 3452]



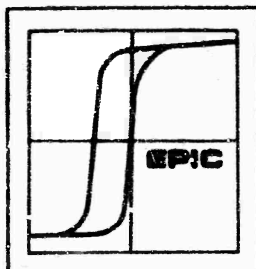
LEAD SULFIDE

ENERGY GAP ( $E_g$ )

<u>Value (eV)</u>	<u>n, <math>10^{18} \text{ cm}^{-3}</math></u>	<u>Type</u>	<u>Sample Single Crystal (100)</u>	<u>Temp.</u>	<u>Ref.</u>
.309 $\pm$ 0.005	5	n	natural, 150 $\mu$ thick	77°K	16127
.307 $\pm$ 0.003	.35	p	epitaxial films; free of substrate 2-5 $\mu$ thick		
.278 $\pm$ 0.002	.35	p	epitaxial film on substrate 2.5 $\mu$ thick		
.280 $\pm$ 0.002	1.1	n	"		
.278 $\pm$ 0.002	1.5	n	"		

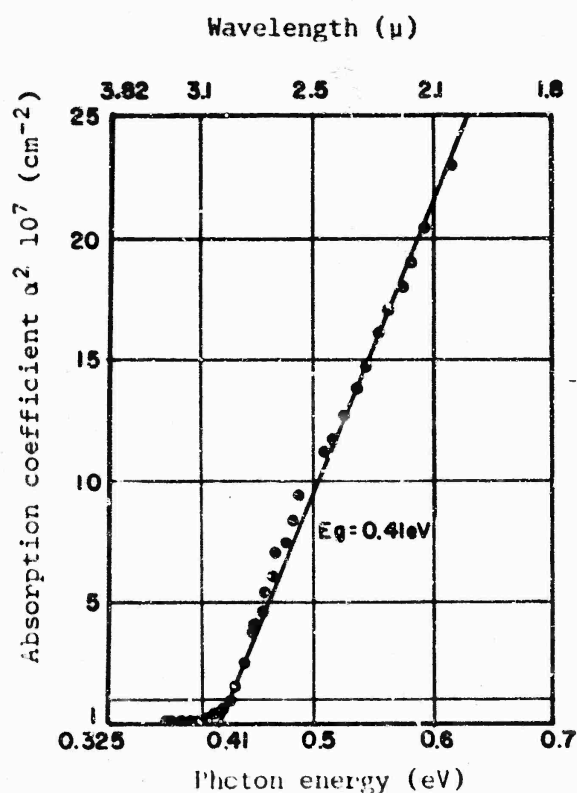
Strain on epitaxial layers acts like impurities to increase energy gap.

<u>Value (eV)</u>	<u>Sample Single Crystal</u>	<u>Measurement Method</u>	<u>Temp.</u>	<u>Ref.</u>
0.308 eV (direct)	Single crystal n-type $n = 3.5 \times 10^{17} \text{ cm}^{-3}$	Faraday rotation	42°K	20567
0.41 (indirect transition)	single crystal cleavage planes on (100) natural and synthetic $n = 10^{17}$ to $10^{19} \text{ cm}^{-3}$	optical absorption at 2 to 4 $\mu$	300°K	577
0.37 (indirect transition)	"	"	"	"
0.34 $\pm$ 2.7 $\times 10^{-4}$	pure, natural, $n = 3.5 \times 10^{15} \text{ cm}^{-3}$ $\rho \approx 3 \Omega \text{ cm}$	Thermal emf conductivity	0°K	19724
0.34 $\pm$ 1.5 $\times 10^{-4}$	"	"	"	"



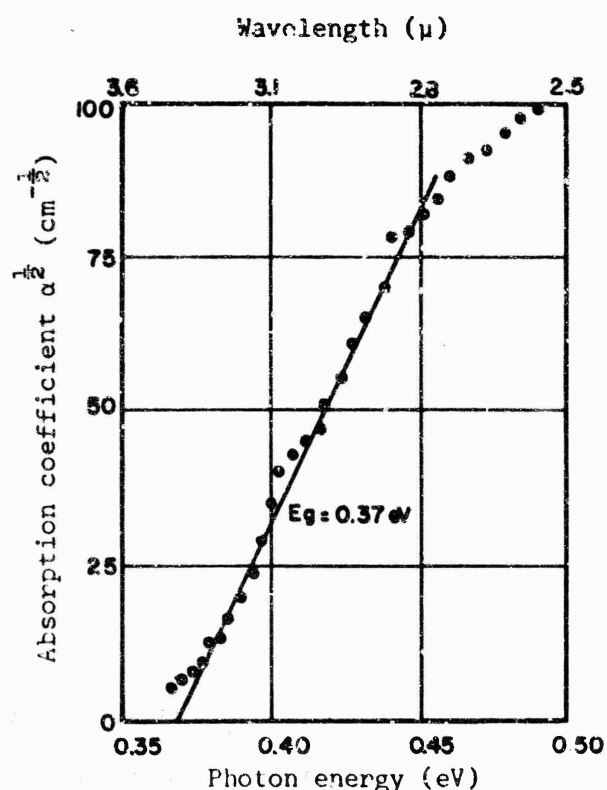
# LEAD SULFIDE

## ENERGY GAP



The absorption coefficient squared as a function of photon energy for indirect transition in lead sulfide at 300°K. Determined from transmission data.

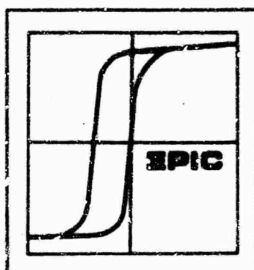
Single crystal lead sulfide, (100) cleaved, natural and synthetic,  $n = 10^{17} - 10^{19} \text{ cm}^{-3}$ . Both transitions are indirect. (See Ref. 22572).



The square root of the absorption coefficient as a function of energy for indirect transitions in lead sulfide at 300°K.

[Ref. 577]





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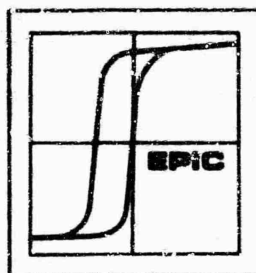
# LEAD SULFIDE

## ENERGY LEVELS

Symbol	Value (eV)	Sample Single Crystal	Measurement Method	Temp. °K	Ref.
$E_0$	0.37	natural synthetic	absorption	300	577
	0.30 (onset of indirect transitions)	(100) cleaved, $n = 10^{17}-10^{19} \text{ cm}^{-3}$		77	
$E_1$	1.3	chemically deposited film	optical absorption	300	3444
	1.3 (smallest vertical transition between valence and conduction band)	calculated for single crystal bulk material	"		22572
$E_1$	1.83	(100) cleavage plane	reflectivity at 2.5-0.05 $\mu$ (calc.)		14189
	1.95	"	"		
	1.88	epitaxial film 0.034 $\mu$ thick	transmission		
	1.85	"	"	77	
$E_2$	3.67	(100) cleavage plane	reflectivity at 2.5-0.05 $\mu$ (calc.)	300	
	3.54	"	"	"	
	3.52	epitaxial film 0.034 $\mu$ thick	transmission		
	3.49	"	"	77	
	3.20	"	maximum in absorption curve	300	
$E_3$	5.3	(100) cleavage plane	reflectivity at 2.5-0.05 $\mu$ (calc.)		
	5.0	epitaxial film 0.034 $\mu$ thick	transmission		
	5.23	"	"		
	5.27	"	"	77	



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## LEAD SULFIDE

### ENERGY LEVELS

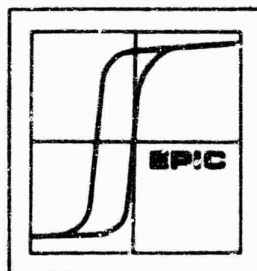
<u>Symbol</u>	<u>Value (eV)</u>	<u>Sample Single Crystal</u>	<u>Measurement Method</u>	<u>Temp. °K</u>	<u>Ref.</u>
$E_4$	8.1	(100) cleavage plane	reflectivity at 2.5-0.05	300	14189
$E_5$	9.8	"	"	"	"
$E_6$	13.9	"	"	"	"

$E_0$ ,  $E_1$ ,  $E_2$ , and  $E_3$  gaps are differences between predominant p-type states,  $E_4$  and  $E_5$  states are gaps between a valence band state and a p-type conduction band.

Analysis indicates that the energy bands are not simple paraboloids around the origin of k-space, but contain various maxima and minima at nonzero k-values. [13554, 22572, 22571] Calculations indicate that the minimum separation between valence and conduction bands ( $E_0$ ) occurs along the (110) direction and not at the center of the Brillouin zone.

[Ref. 22571]

<u>Symbol</u>	<u>Value (eV)</u>	<u>Dopant</u>	<u>Sample (single crystal)</u>	<u>Temp. °K</u>	<u>Ref.</u>
$E_A$	0.4	Ag	p-type, $n = 10^{18} \text{ cm}^{-3}$	1200	3679
	0.45			1100	
	0.45			1000	
	~0.4			800	
	~0.3			300	
$E_D$	0.14	Bi	n-type, $n = 10^{18} \text{ cm}^{-3}$	1000-1200	
	~0.10			800	
	~0			300	



# LEAD SULFIDE

## ENERGY LEVELS

Spin-Orbit Split    The single-electron atomic spin-orbit splitting for p and d states in lead and sulfur, have been estimated from the atomic energy levels of the neutral and singly ionized atoms. It is assumed that electrons in the valence and conduction bands at L spend 40% time on the lead atom and 60% on the sulfur atom.

$L_3 = 0.06 \text{ eV}$

$L_3' = 0.96 \text{ eV}$

Conduction band edge is at L point (111 edge) of the Brillouin zone. [Ref. 16104]

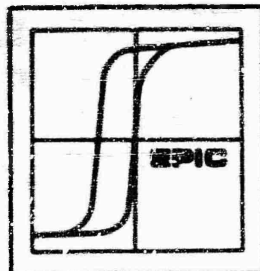
Symbol	Value (eV)	Dopant	Sample	Temp. °K	Ref.
$E_D$	0.04	Cu	single crystal, p-type, when copper-diffused becomes n-type	77-300	14461

$E_D$	0.02	Cu	single crystal, n-type	300	22594
$E_D$	0.03	Ni	single crystal, n-type $n = 5 \times 10^{18} \text{ cm}^{-3}$	"	22593

Symbol	Value (eV)	Dopant	Type	Sample (single crystal)	Test Method	Temp. °K	Ref.
$E_D$	0.02 CB	Excess Pb	n	synthetic, $n = 8 \times 10^{16} - 8 \times 10^{18} \text{ cm}^{-3}$	PEM & PC	140-300	7170
$E_D$	0.037 VB	Excess S	p	" "	" "	" "	"

$E_D$  Donor level

$E_A$  Acceptor level

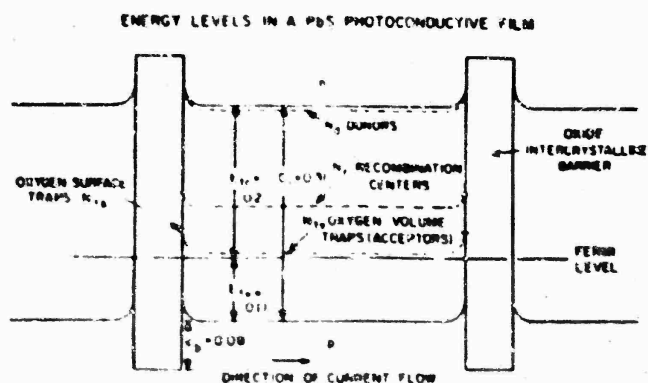


## LEAD SULFIDE

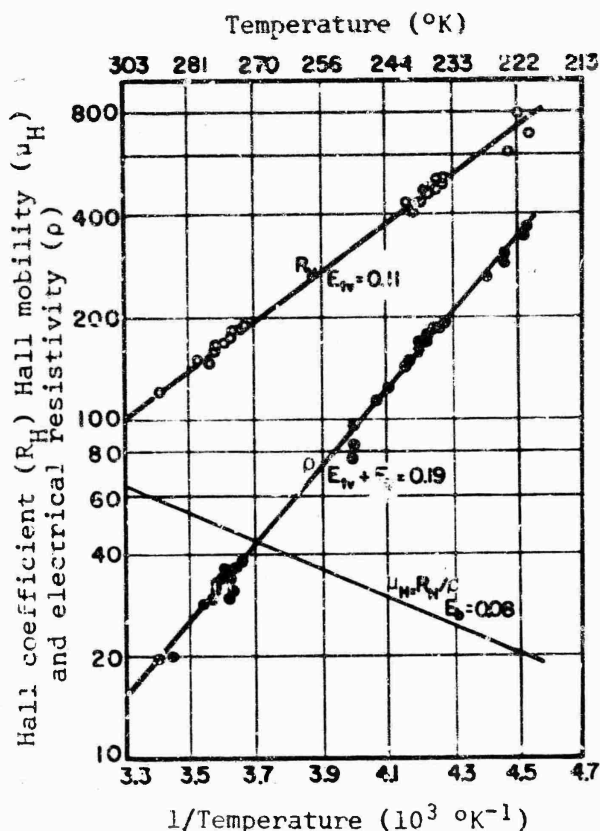
### ENERGY LEVELS

Hall coefficient, resistivity, and Hall mobility for a p-type lead sulfide film as a function of reciprocal temperature. The films comprise lead sulfide crystallites with intercrystalline barriers of 10 Å thickness.

Energy levels of traps and barriers are determined from slope of these curves. Oxygen appears to provide deep electron traps, although a good part of the photoconductivity is the result of surface states in the polycrystalline material.



Energy levels in a PbS photoconductive film



$$E_A = N_{tv}, \text{ oxygen volume traps} = 0.11 \text{ eV}$$

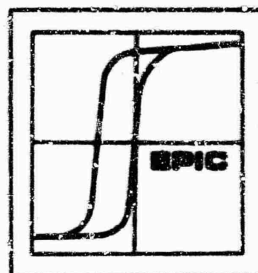
$$E_{tv} = \text{traps above valence band} = \text{Fermi level} = 0.11 \text{ eV}$$

$$E_b = \text{barrier level} = 0.08 \text{ eV}$$

$$E_{tc} = 0.2 \text{ eV} = \text{traps below conduction band}$$

$$E_{tc} + E_{tv} = E_i = E_g = 0.31 \text{ eV}$$

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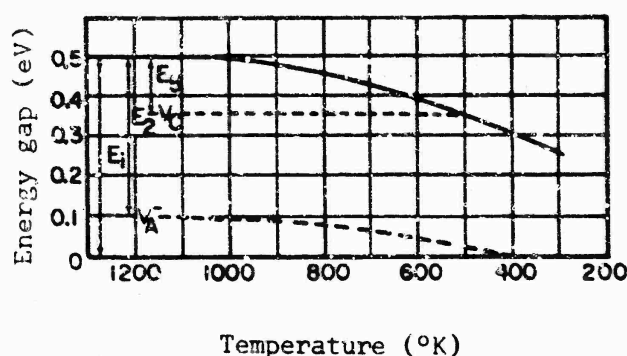


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## LEAD SULFIDE

### ENERGY LEVELS



The variation with temperature of the band width and the depth of the various localized levels for PbS single crystals.

$E_1$  is the energy gap

$V_C$  is the bismuth (donor) level

$V_A$  is the silver (acceptor) level

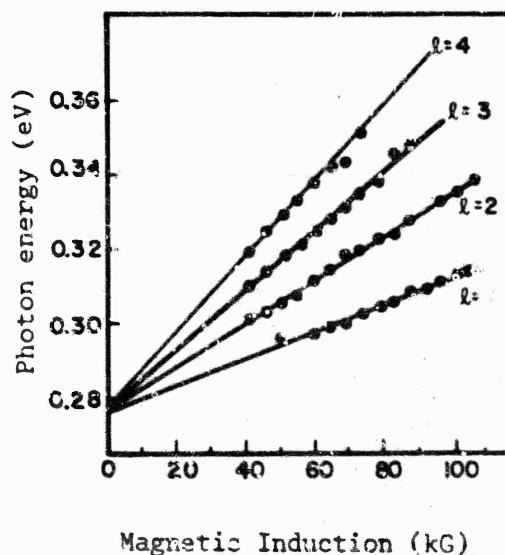
( $V_A$  and  $V_C$  are the levels;  $E_2$  and  $E_3$  are the gaps or level differences)

[Ref. 3679]

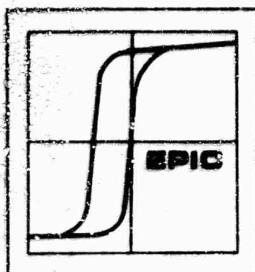
The energy levels of the Landau transitions are plotted as a function of the magnetic induction for a single crystal p-type epitaxial film 77°K. The value for the energy gap, 0.28 eV, obtained from extrapolation of the line to zero field, and the value for the reduced effective mass obtained from the line spacing, are characteristic of the strained crystal.  $n = 3.5 \times 10^{17} \text{ cm}^{-3}$ . Field parallel to (100). (See page 44)

$\ell$  represents the quantum number for a given Landau level as required by the selection rules for interband transitions.

[Ref. 16127]







LEAD SULFIDE

GYROMAGNETIC PROPERTIES

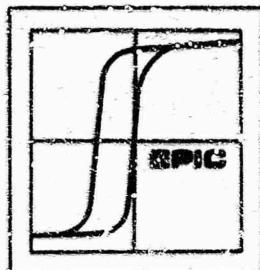
Effective g-factor for valence ( $g_v$ ) and conduction ( $g_c$ ) bands.

Symbol	Value	Sample Single Crystal	Test Measurement	Temp.	Ref.
$g_c$	$10.0 \pm 1.5$	epitaxial films 5 microns thick, p-type, $n = 3.5 \times 10^{18} \text{ cm}^{-3}$	Faraday rotation	77°K	16127
$g_v$	$-8.5 \pm 1.5$	" "			
$g_v$	-3.8	epitaxial films 5 microns thick, n-type, $n = 1.1 \times 10^{18} \text{ cm}^{-3}$			
$g_c$	+5.3	" "			

Band edge longitudinal g-factor ( $g_{||}$ )

$g_c$	$12 \pm 3$		Calculated from spin-splitting of Landau level	4°K	24930
$g_v$	$13 \pm 3$		"	"	"

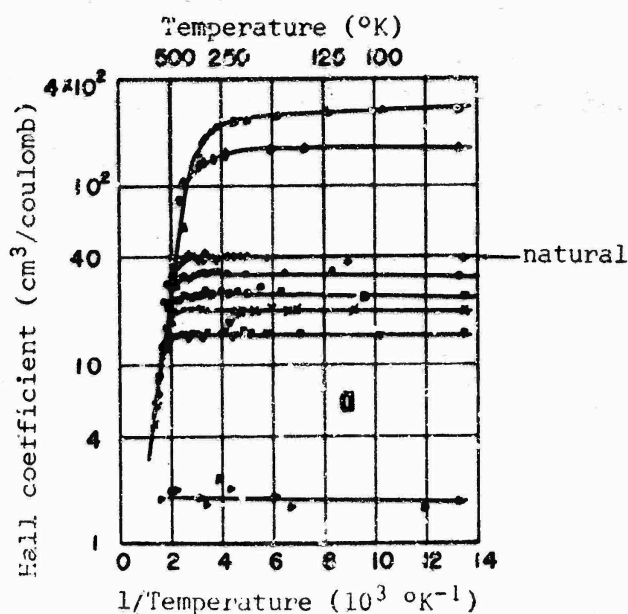




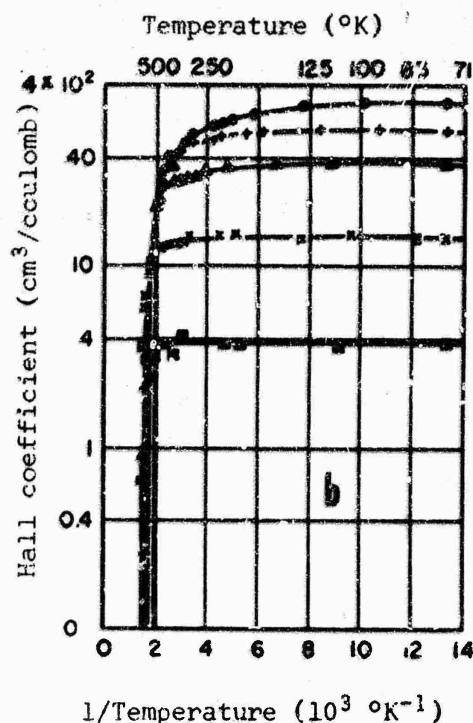
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# LEAD SULFIDE

## HALL COEFFICIENT



Symbol	$n, 10^{16} \text{ cm}^{-3}$
▲ 18a	2.8
◆ 23a	4.5
+ natural	.18
● 11a	.22
■ 7a	.29
x 1b	.36
▼ 4a	.48
► synthetic	.042



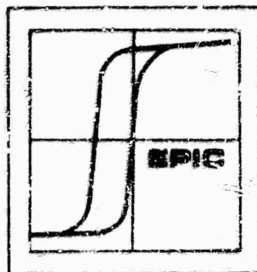
Symbol	$n, 10^{16} \text{ cm}^{-3}$
● 20b	8.8
+ 23c	.13
▲ 23b	.19
x 2a	.5
■ synthetic	.02

Hall coefficient as a function of reciprocal temperature for natural and synthetic lead sulfide single crystals. The natural n-type crystals were held at 500°C in sulfur vapour for 20 hours at various pressures from  $3 \cdot 10^{-5}$  to 0.3 mm Hg and then quenched to 20°C. The resultant n-type (excess lead) samples are shown in (a) and the p-type (excess sulfur) samples are shown in (b). Carrier concentrations were taken from [Ref. 288]

The treatment is reversible; the crystals may be changed from n- to p-type and back again. Measurements are reproducible.

Curve 1 on both graphs represents data taken on untreated synthetic crystals, prepared as n- and p-type samples. The curve marked "natural" (+) is for the untreated natural lead sulfide crystals used in the experiment.

[Ref. 3612]



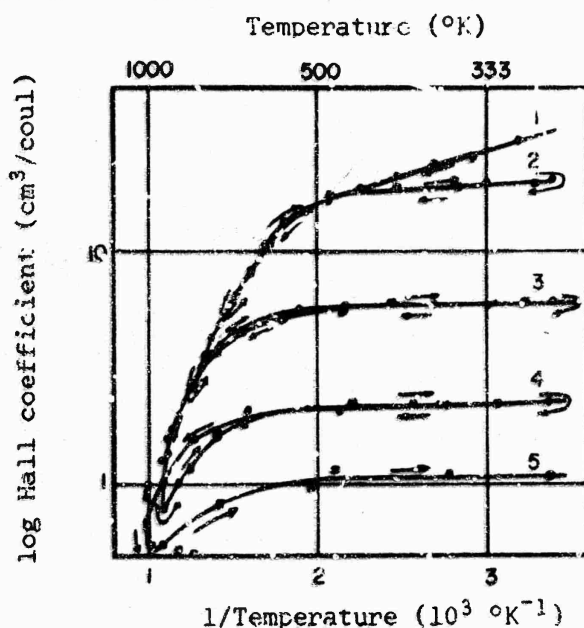
## LEAD SULFIDE

### HALL COEFFICIENT

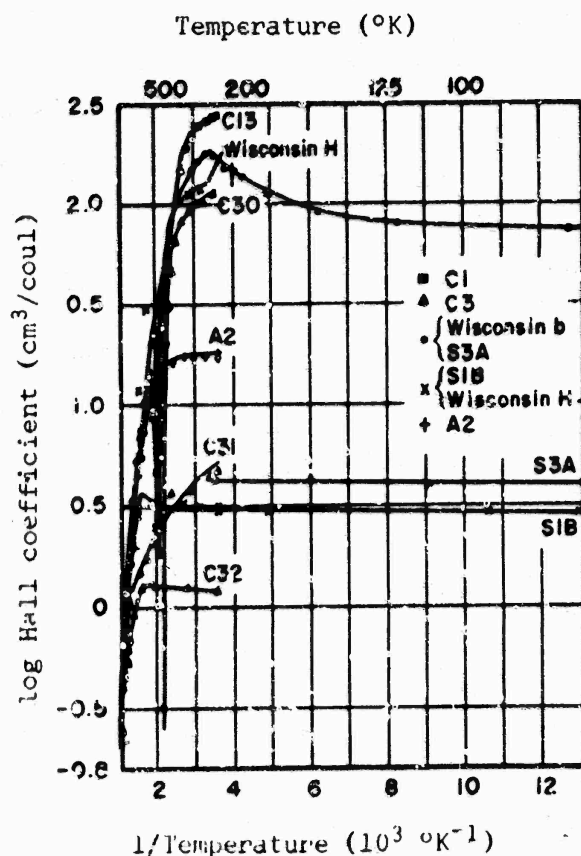
Hall coefficient as a function of reciprocal temperature for single crystal lead sulfide, natural n-type, heated in argon atmosphere. Curve 1 is heated to 680°K and curve 2 is the cooling curve for the sample brought down to 300°K and then heated to 788°K. Curve 3 is the sample brought to 919°K and curve 4 is held at 1023°K for one hour. The sulfur loss at high temperatures produces a very high concentration of electrons (lead) so that curve 5 levels off at  $1 \text{ cm}^3/\text{coul}$ .

- heating curve
- cooling curve

curves show composition changes as a result of heating.

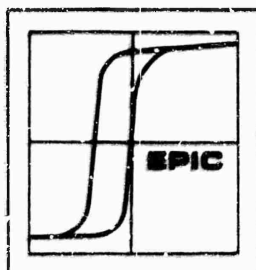


[Ref. 2137]



Log Hall coefficient as a function of reciprocal temperature for single crystal natural lead sulfide, cleaved (100), measurement made in an argon atmosphere.  $n = 10^{16}$  to  $10^{18} \text{ cm}^{-3}$ . Changes in slope did not occur up to 850°K, at this point, sulfur loss is initiated.

[Ref. 2883]



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## LEAD SULFIDE

### HALL COEFFICIENT

Hall coefficient as a function of reciprocal temperature in single crystal n-type lead sulfide epitaxial films.

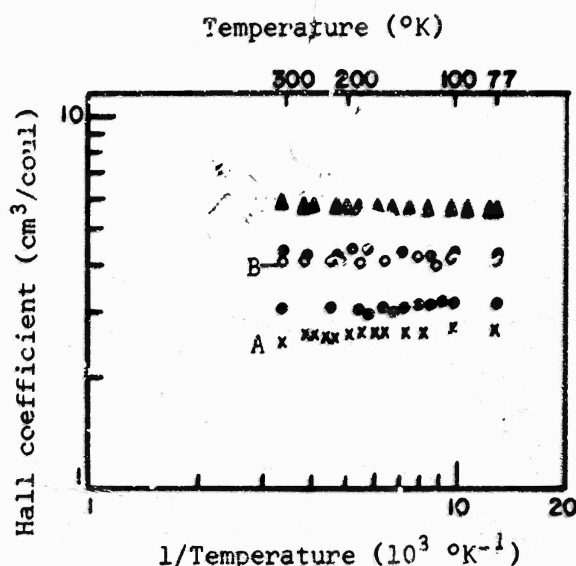
- , x, is 1.26 microns thick
- , is 4.69 microns thick

The other films are of the same order of thickness.

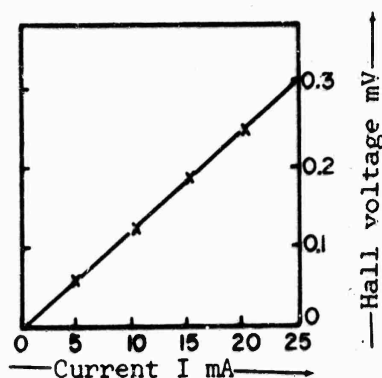
$$n_n = 2 \times 10^{18} \text{ cm}^{-3}$$

A films show bulk properties

B films show defect structure properties



[Ref. 22079]

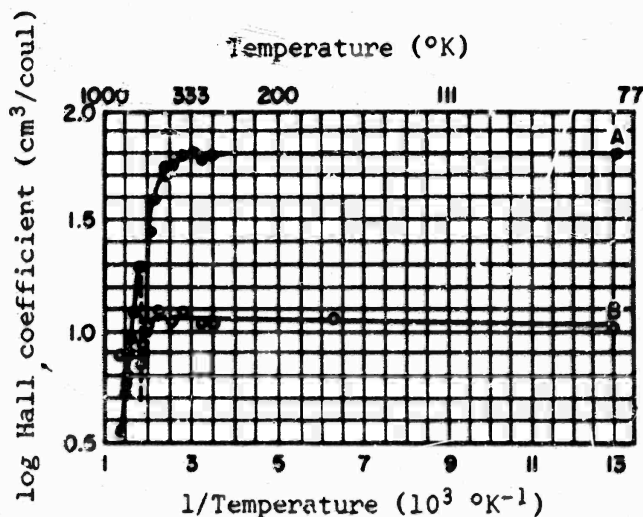


Hall voltage as a function of electrical current at 300°K for natural n-type single crystal lead sulfide  $n = 10^{16} - 10^{18} \text{ cm}^{-3}$ .

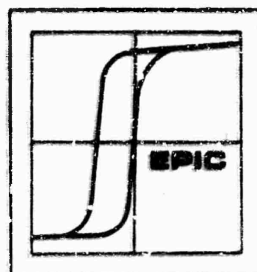
[Ref. 22574]

Log Hall coefficient as a function of reciprocal temperature for 2 samples p-type, compressed powder lead sulfide sintered at 1100°K in  $\text{H}_2\text{S}$  gas.

In sintered lead sulfide conductivity may be affected by inter-crystalline barriers, at higher temperatures conductivity behaviour is similar to that of single crystals. For this reason Hall coefficient data must be combined with the resistivity measurements.



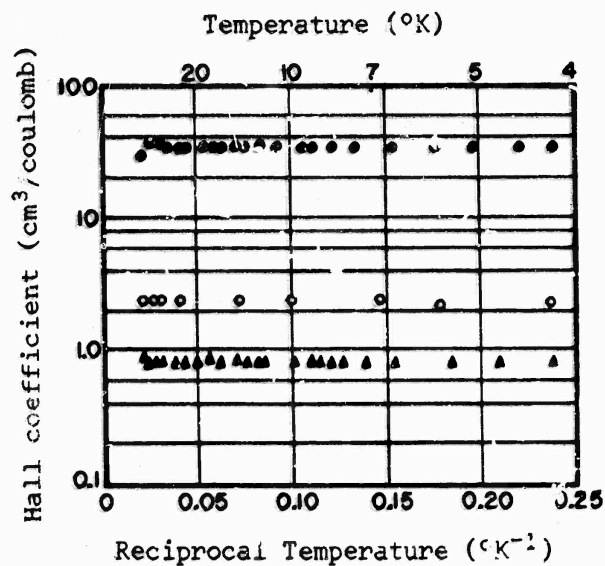
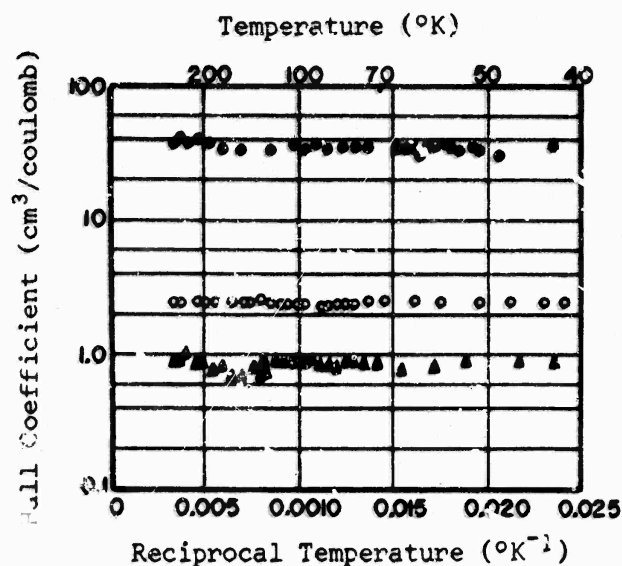
[Ref. 3904]



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# LEAD SULFIDE

## HALL COEFFICIENT

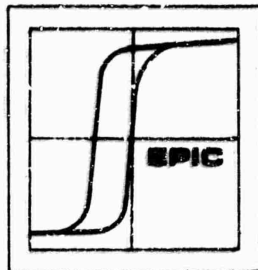


Hall coefficient as a function of reciprocal temperature for single crystal lead sulfide. At these temperatures the Hall coefficient has levelled off and is not affected by temperature change.

Sample	Type	$n, 10^{18} \text{ cm}^{-3}$
● natural	n-	0.2
○ synthetic	n-	7.0
▲ synthetic	p-	3.0

[Ref. 776]

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## LEAD SULFIDE

### IRRADIATION

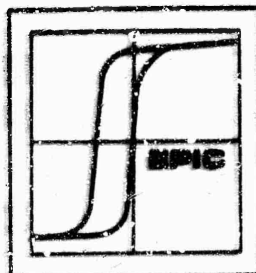
The photoconductivity of lead sulfide films approximately 0.6 microns thick, irradiated by argon ions at 100-400 eV decreased sharply and finally became zero. Heating in air restored the photoconductivity. Single crystal epitaxial films behaved similarly to polycrystalline layers. Evidently the ions caused desorption of the gaseous adsorbed surface layer. [Ref. 13276]

At approximately 100 eV electron irradiation at a critical angle of incidence, an induced emf of 1 volt is achieved in polycrystalline lead sulfide films. Photon energy increases this emf by an additional photovoltaic effect. [Ref. 22660]

Cobalt-60 gamma radiation of lead sulfide infrared detectors caused immediate deterioration of performance. After a total dose of about  $10^7$  roentgens, the sensitivity is reduced to about 20% of the initial value. [Ref. 22864]



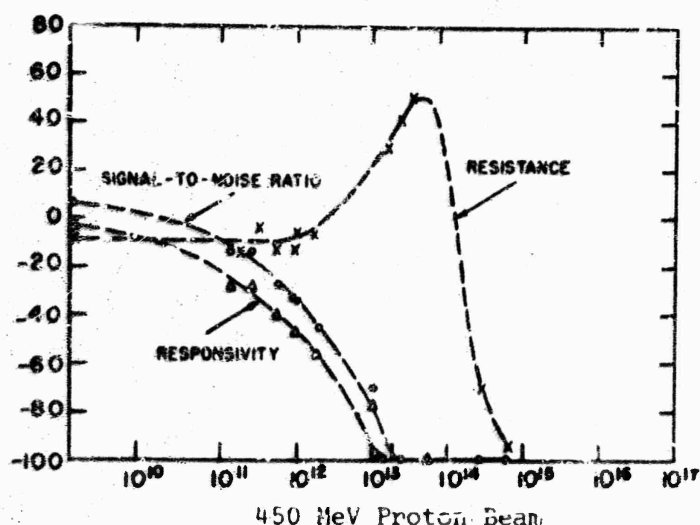
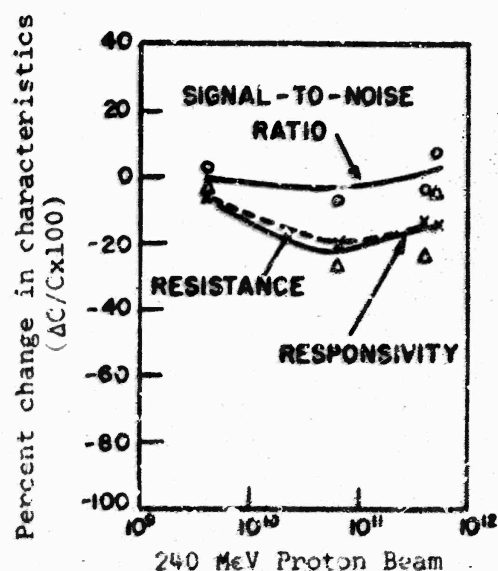
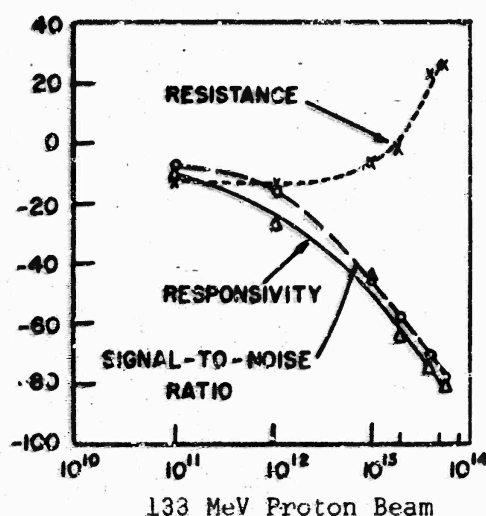
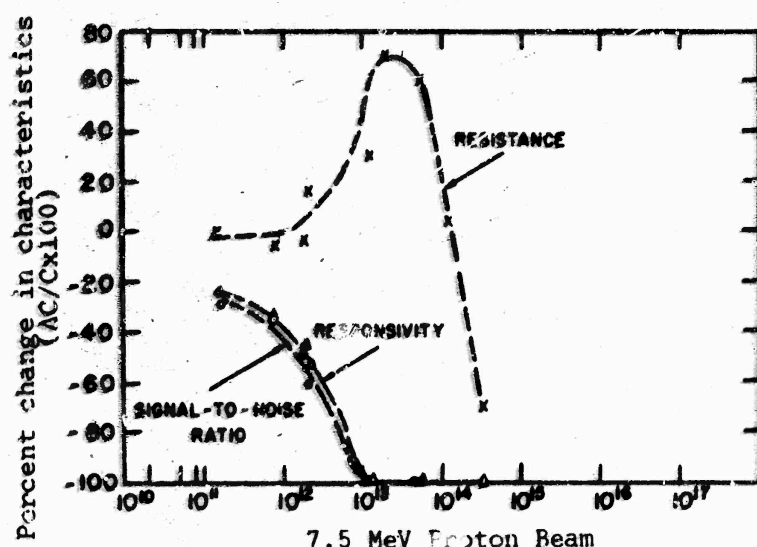
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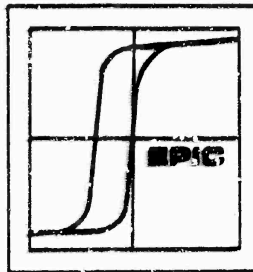
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# LEAD SULFIDE IRRADIATION

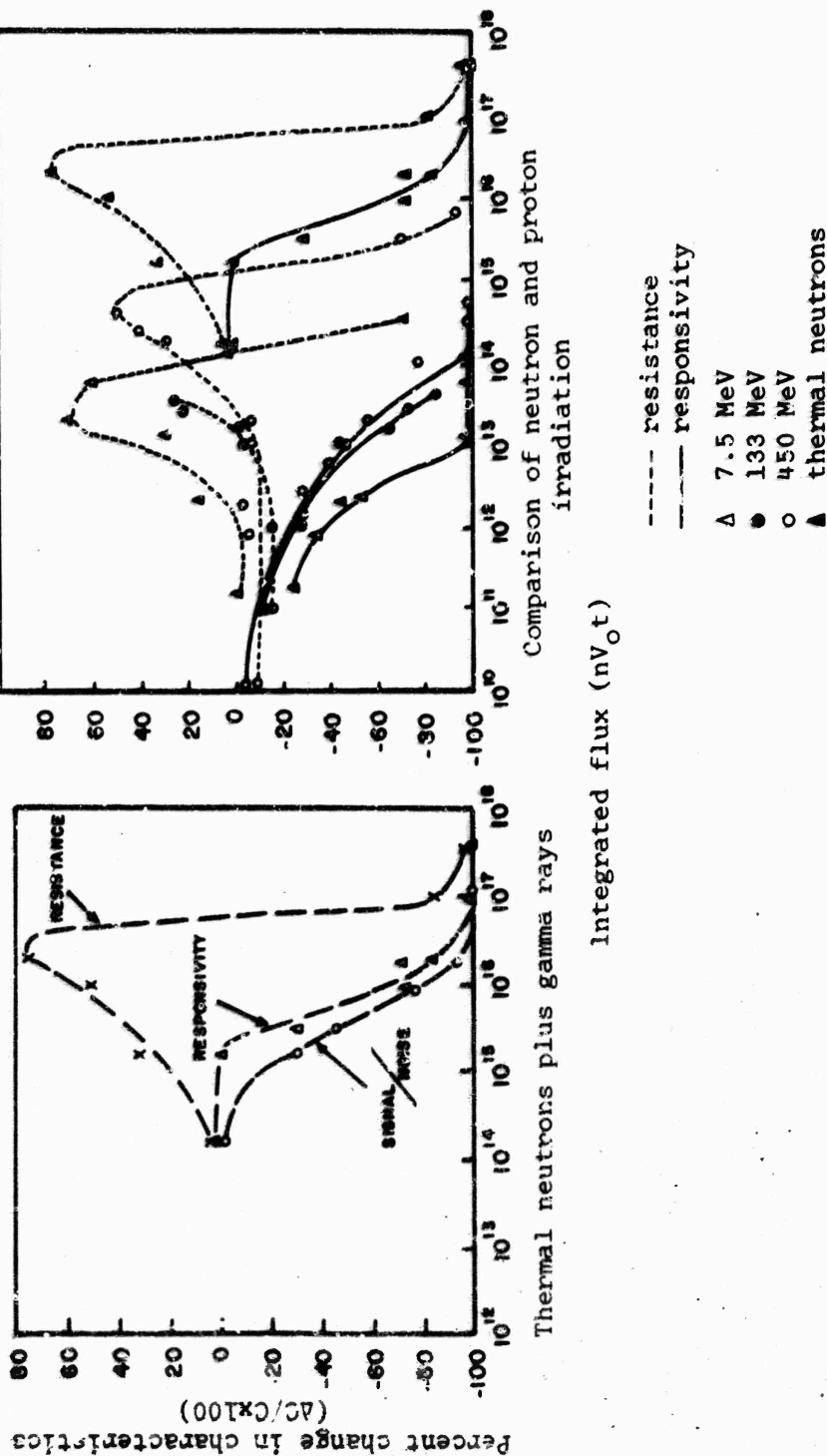


Change in commercial lead sulfide film cell characteristics (spectral response) as a function of integrated proton flux for several proton beam irradiation values.

[Ref. 7774]

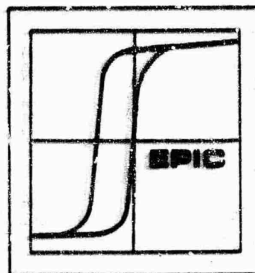


LEAD SULFIDE  
IRRADIATION



Change in commercial lead sulfide film cell characteristics (spectral response) as a function of varied irradiation. Type of damage from neutron irradiation is similar to that from proton bombardment, although higher neutron flux is required to initiate damage.

[Ref. 7774]

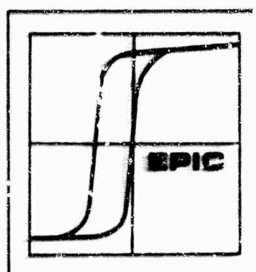


LEAD SULFIDE

LIFETIME

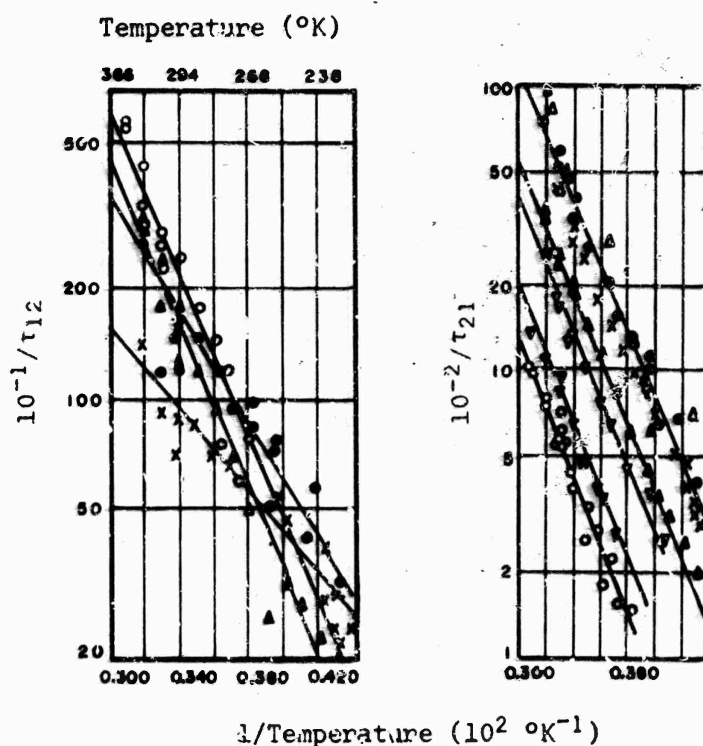
Symbol	Value (μsec)	Carrier Concentration $n, 10^{15} \text{ cm}^{-3}$	Sample	Test Measurement	Temp.	Ref.
$\tau$	63	-	single crystal natural and synthetic, (100) cleaved $n = 3 \times 10^{15} \text{ cm}^{-3}$	radiation recombination	300°K	577
$\tau$	20-560 (photoconductivity decay time constant)	-	films, 0.5 microns thick, highly photosensitive	photoconductive dc and microwave frequencies		284
$\tau_p$	15-20	3.5	pure single crystal, natural lead sulfide	electrical		19724
	50-60	1.7	"	"		"
		2.1	"	"		"
$\tau$	40	-	-	calculated from radiative recombination in single crystals		149

$\tau_p$  = hole lifetime



LEAD SULFIDE

LIFETIME



Reciprocal of lifetime as a function of reciprocal temperature for lead sulfide films, measurements made in nitrogen atmosphere.

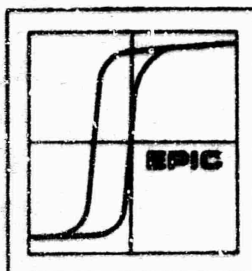
$\tau_{12}$  is the rate of hole capture

$\tau_{21}$  is the rate of hole emission from the surface

Symbol	$n, 10^{16} \text{ cm}^{-3}$
$\Delta, x$	7.4
$\bullet$	3.7
$\blacktriangle$	1.3
$\nabla$	5.4
$\nabla, o$	4.0

[Ref. 3580]

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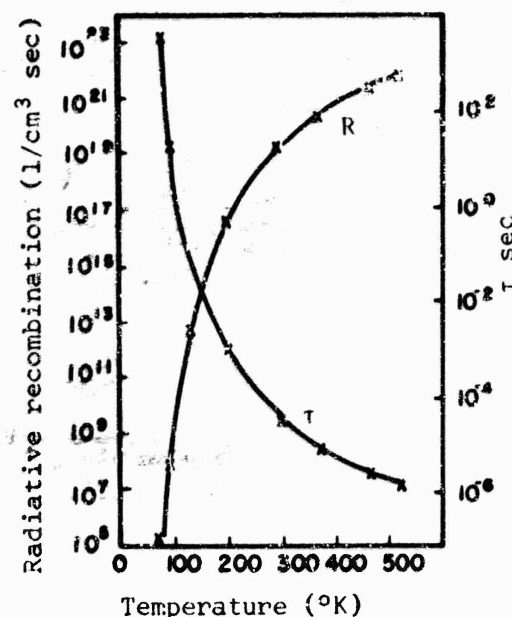
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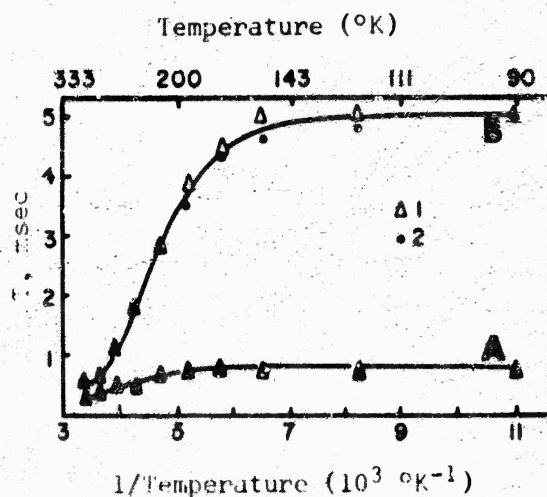
# LEAD SULFIDE

## LIFETIME

The temperature dependence of the radiative recombination and lifetime for lead sulfide. Optical absorption and luminescence measurements were used to calculate lifetime at 77-522°K.



[Ref. 14453]



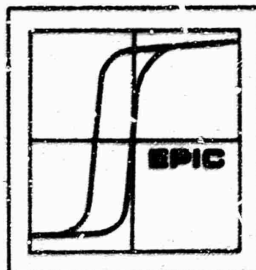
Lifetime values as a function of reciprocal temperature in a chemically deposited lead sulfide film, 0.5 microns thick were measured by two methods:

1. Resonance at 10 Gc
2. Direct current

A. at 1 mW/cm² illumination, lifetime was practically independent of temperature. B. at 0.1 mW/cm², lifetime increased ten times as the temperature decreased to 90°K. Illumination changes the barrier height between the crystallites so that a secondary photocurrent is produced.

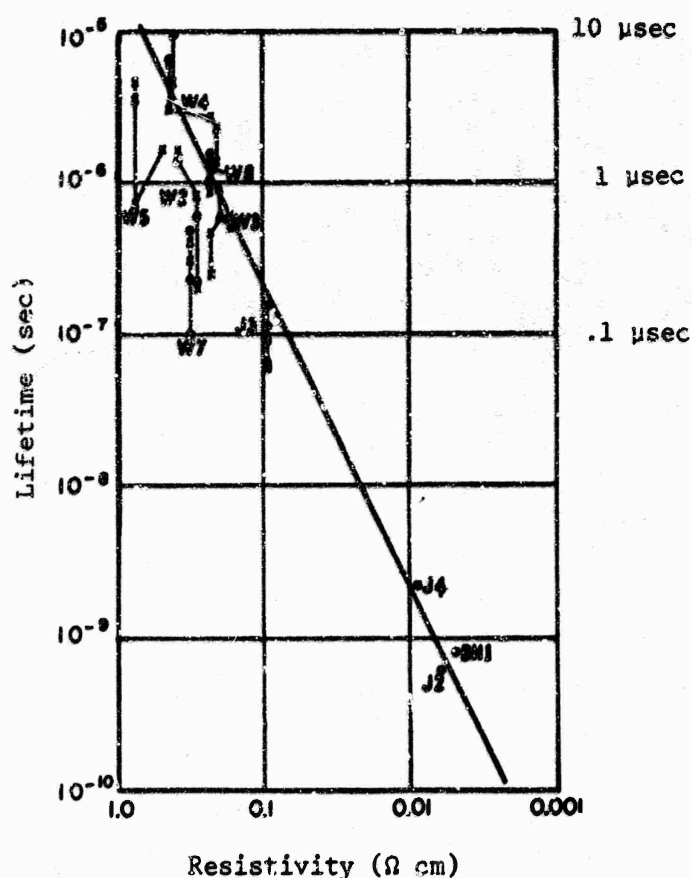
[Ref. 3863]





# LEAD SULFIDE

## LIFETIME



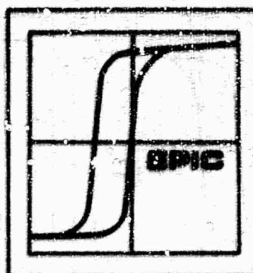
Lifetime as a function of electrical resistivity in single crystal lead sulfide determined by two photoelectronic methods.

- photoelectromagnetic effect (PEM)
- x photoconductive/PEM
- light spot
- ▲ rise time

Values calculated for  $\mu = 800 \text{ cm}^2/\text{V sec}$  in the several samples.

[Ref. 2835]

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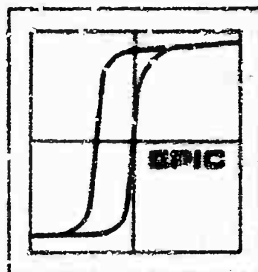
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LEAD SULFIDE

MAGNETIC SUSCEPTIBILITY

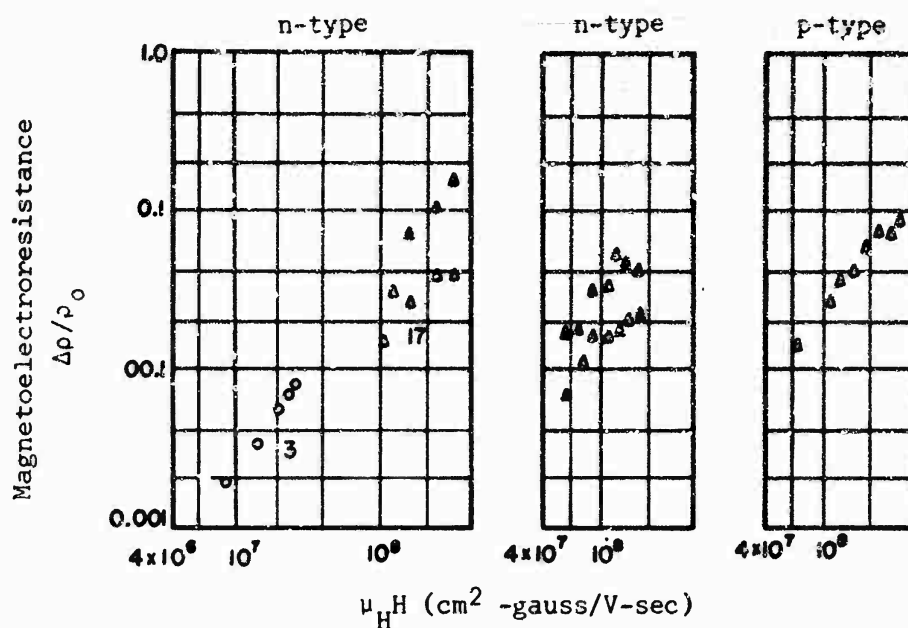
<u>Symbol</u>	<u>Value (cm<sup>3</sup>/g)</u>	<u>Ref.</u>
X	-0.37 x 10 <sup>-6</sup> emu	7359



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# LEAD SULFIDE

## MAGNETOELECTRIC PROPERTIES

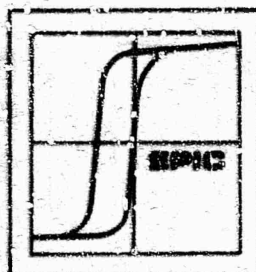


Transverse and longitudinal magnetoresistance in single crystal synthetic lead sulfide as a function of the mobility-magnetic field strength product.  $n \sim 10^{16} \text{ cm}^{-3}$ . Results are very similar for n- and p-type samples; saturation effects were seen at higher fields at 4.2°K.

- transverse, 77.4°K
- △ transverse, 4.2°K
- ▲ longitudinal, 4.2°K

[Ref. 783]

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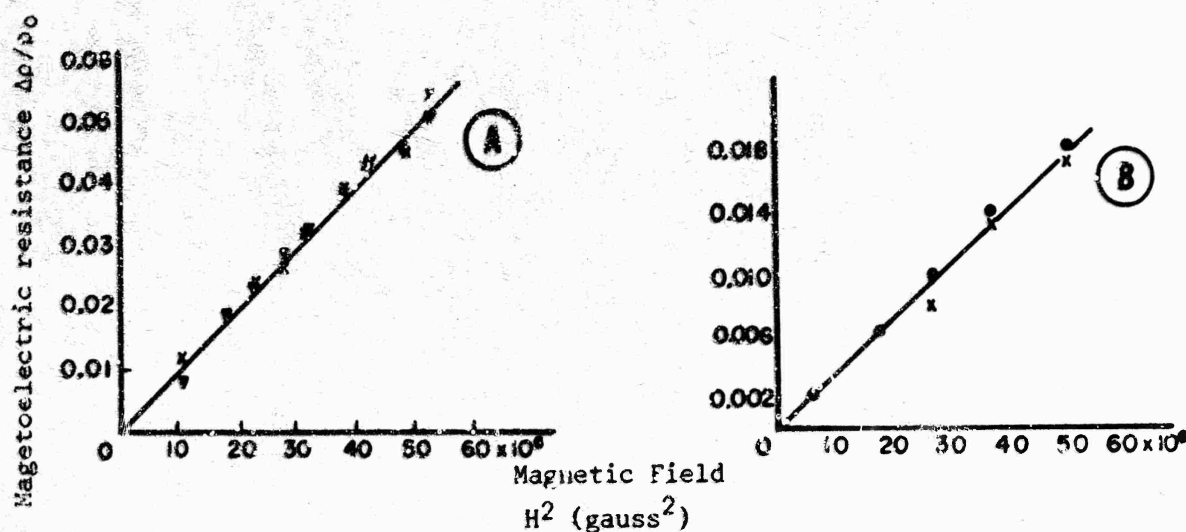


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# LEAD SULFIDE

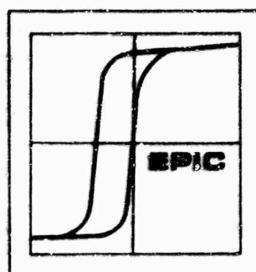
## MAGNETOELECTRIC PROPERTIES



Transverse magnetoelectric resistance as a function of magnetic field squared for natural, single crystal lead sulfide.

	Temp.	Type	$n, 10^{16} \text{ cm}^{-3}$
A	108°K	p	2,
B	93°K	n	~ 5.

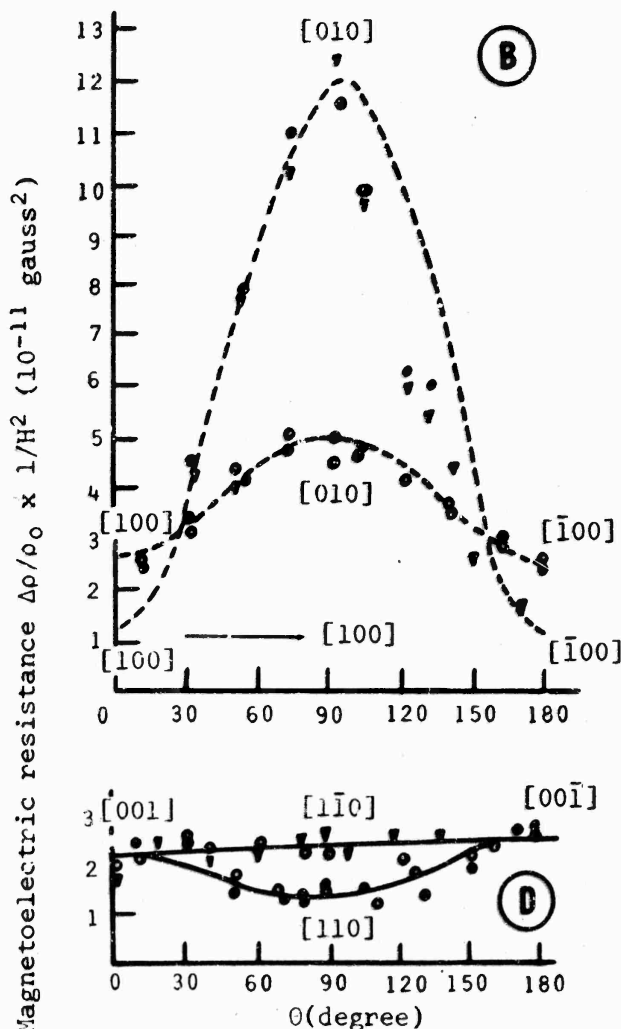
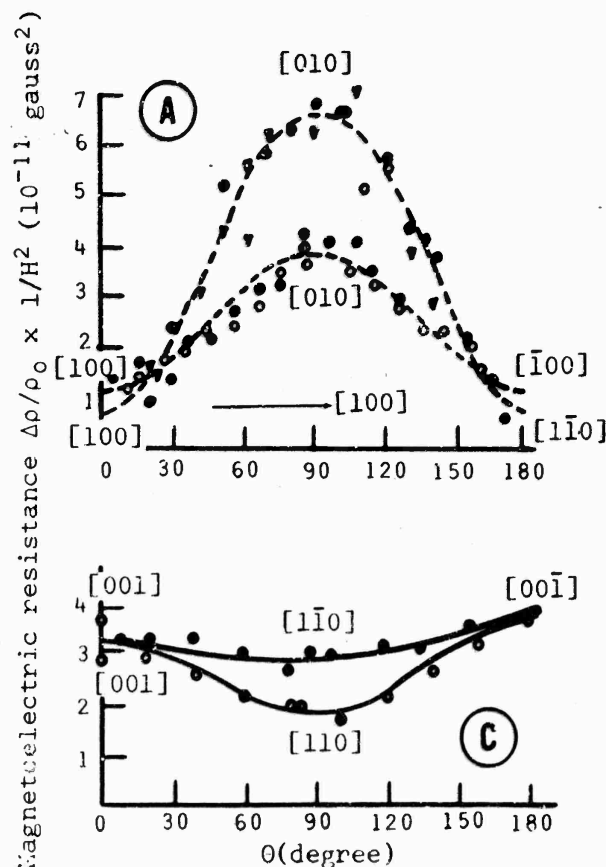
[Ref. 259]



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LEAD SULFIDE

MAGNETOELECTRIC PROPERTIES

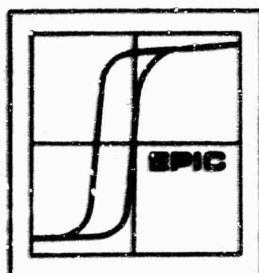


Magnetoelectric resistance ratio times the reciprocal of the field squared is reported as a function of the angle between current and field. Samples are natural galena single crystals of lead sulfide. The applied field directions are indicated.

Graph	Temp. (°K)	Type	Current Direction	$n, 10^{16} \text{ cm}^{-3}$
A	200	p-	(100)	2.0
B	93	p-	(100)	2.0
C	200	p-	(110)	1.4
D	"	n-	(110)	12.0

[Ref. 259]





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**LEAD SULFIDE**

**MOBILITY**

<u><math>\mu</math> (<math>\text{cm}^2/\text{Vsec}</math>)</u>		<u>Sample (single crystal)</u>	<u><math>n, \text{cm}^{-3}</math></u>	<u>Ref.</u>
<u>77.4°K</u>	<u>4.2°K</u>			
6040	14400	n-type, synthetic	$10^{18}$	783
11000	68500	"		
8750	40200	"		
15000	80000	p-type, synthetic		

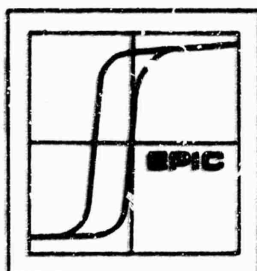
<u><math>\mu_{\text{dc}}</math></u>	<u><math>\mu_{\text{dark}}</math></u>	<u><math>\mu_{\text{photo}}</math></u>	<u>Sample</u>	<u>Test Conditions</u>	<u>Temp.</u>	<u>Ref.</u>
9.4	19	27	Photosensitive films chemically deposited and generally p-type $\sim 0.5 \mu$ thick, $n \sim 10^{17} \text{ cm}^{-3}$ $\rho = .1 \text{ to } .5 (\Omega \text{ cm})^{-1}$	$10^4 - 10^{10} \text{ cps}$ and 6 kOe	300°K	284
8.9	8.3	11				
9.2	16	21				
8.0	7.8	24				
6.7	17	19				

$\mu_{\text{dark}}$  dark mobility at microwave frequencies ( $\text{cm}^2/\text{Vsec}$ )

$\mu_{\text{photo}}$  photoconductive mobility at microwave frequencies "

$\mu_{\text{dc}}$  direct current mobility at 3V "

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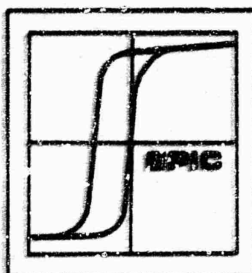
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LEAD SULFIDE

MOBILITY

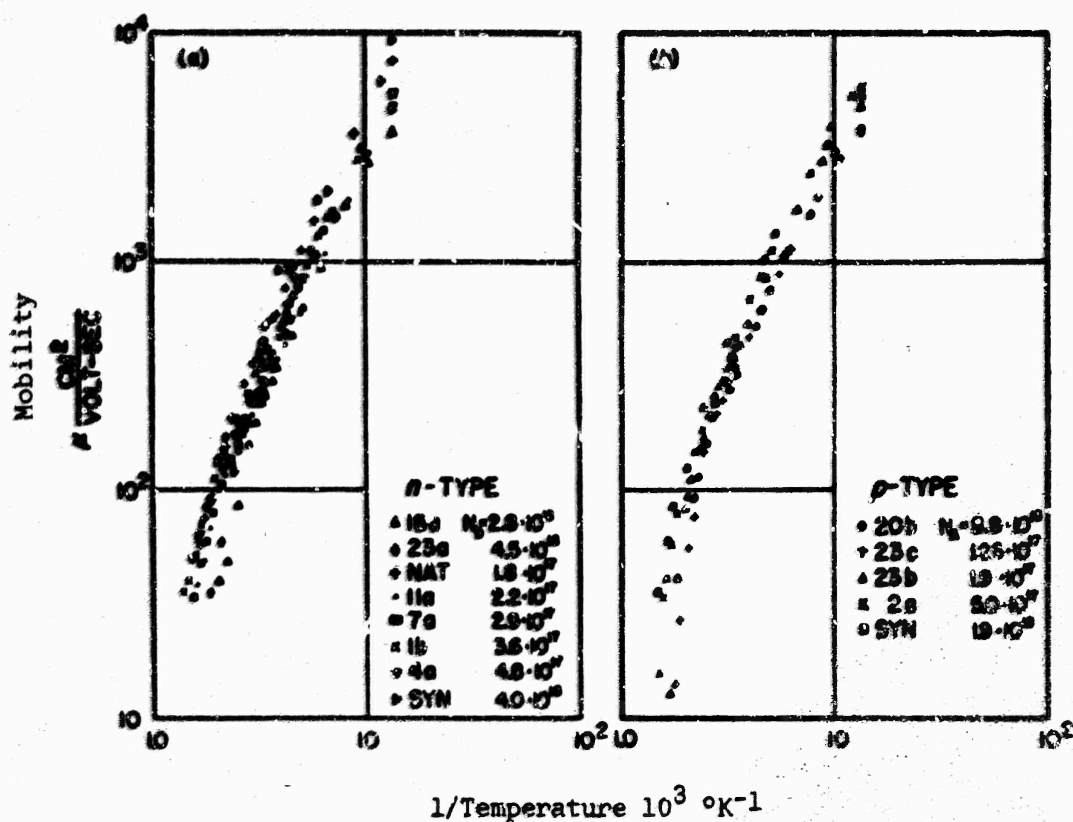
<u>300°K</u>	<u>77°K</u>	<u>Sample (single crystal)</u>	<u>n, (10<sup>17</sup>cm<sup>-3</sup>)</u>
700	13 500	Synthetic	20
500	6000	Natural	5
500	9000	Epitaxial film	20
10	<1	Nonepitaxial film	2

[Ref. 22079]



# LEAD SULFIDE

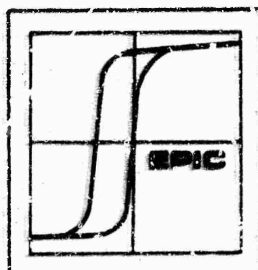
## MOBILITY



Mobility as a function of reciprocal temperature in single crystal n- or p-type lead sulfide samples. Points are derived from electrical measurements on natural and synthetic crystals. The carrier concentrations are shown on the graphs.  $\mu = \mu_0 T^{-2.5}$  at 100-700°K.

Resistivity and Hall measurements for the same samples are given in [Ref. 3612]

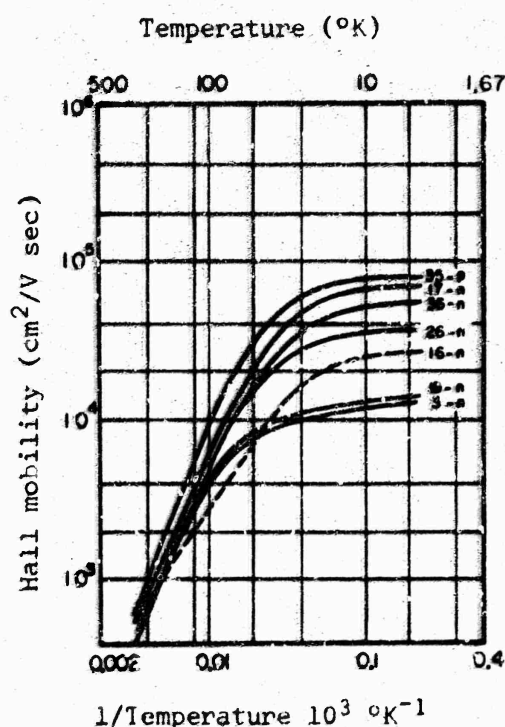
[Ref. 288]



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# LEAD SULFIDE

## MOBILITY



Mobility as a function of reciprocal temperature in single crystal lead sulfide.

No.	Sample	Type	n, 10 <sup>18</sup> cm <sup>-3</sup>	μ, cm <sup>2</sup> /V sec		
				295°K	77.4°K	4.2°K
35	syn.	p	2.66	621	15000	80000
17		n	4.25	515	11000	68500
36			7.45	523	8520	55600
26			4.63	572	8750	40200
16			27.2	500	4160	26800
19	nat.		.184	386	6030	15400
3	"		.164	431	6040	14400

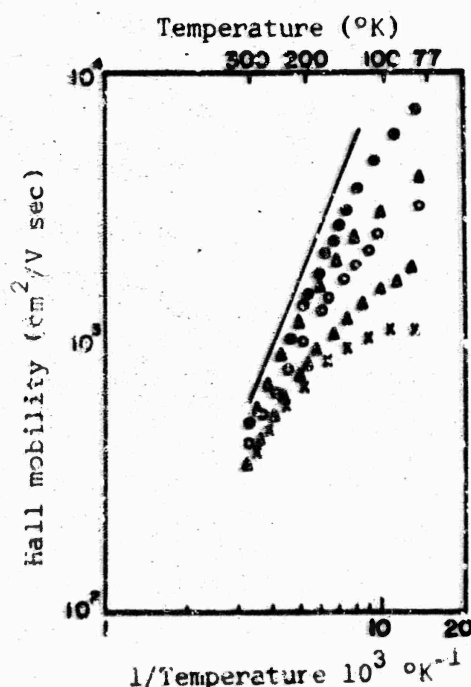
[Ref. 776]

Mobility as a function of reciprocal temperature in single crystal epitaxial lead sulfide films.  
n = 2 x 10<sup>18</sup> cm<sup>-3</sup>.

### Film Thickness

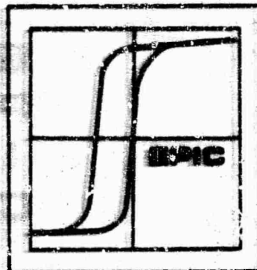
- 1.3 μ
- 4.7 μ
- x this films shows defect structure properties. The others have bulk single crystal properties.

— typical bulk behavior



[Ref. 22079]

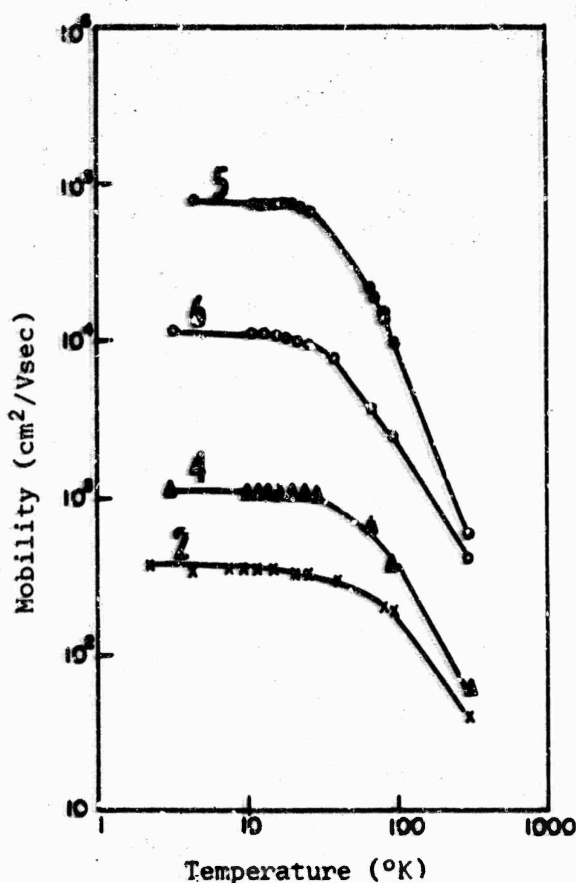




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# LEAD SULFIDE

## MOBILITY

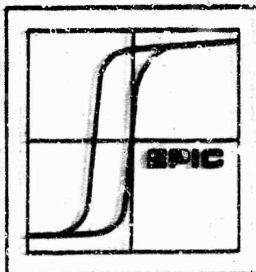


Mobility as a function of temperature in a single crystal lead sulfide.

Sample	No.	Type	$n, 10^{17} \text{ cm}^{-3}$	Sample
x	2	n-	5.9	natural
▲	4	n-	85.	"
•	5	p-	0.17	synthetic
o	6	p-	0.018	silver-doped

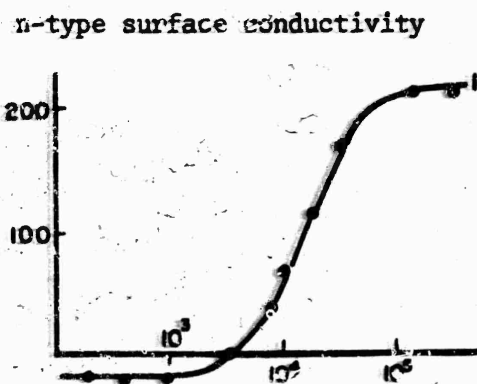
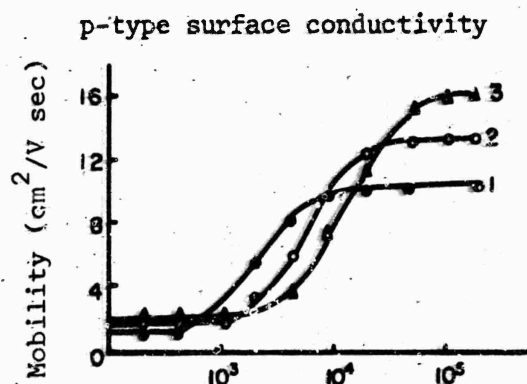
[Ref. 285]





# LEAD SULFIDE

## MOBILITY



Frequency (cps)

Effective mobility at 300°K as a function of frequency in photosensitive lead sulfide films deposited in vacuum. Maximum field of 5000 v/cm.

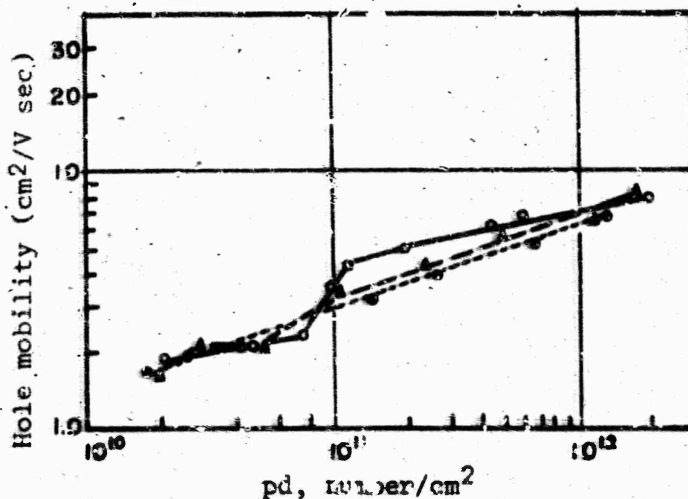
- 1) dark mobility
- 2) mobility under illumination,  $I'$
- 3) mobility under illumination,  $I''$   
 $I'' > I'$

$I$  = intensity in visible range

[Ref. 6093]

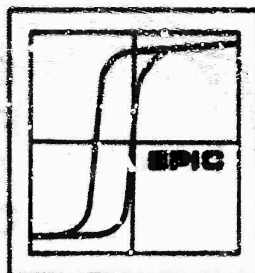
Mobility as a function of hole carrier concentration in photosensitive lead sulfide films about 50 microns thick.  $pd$  is the carrier concentration times single crystal film thickness. Measurements are taken at about the same temperature but at three wave lengths.

- $T = 195^\circ K, \lambda = 2.12 \mu$
- $T = 192^\circ K, \lambda = 0.8 \mu$
- △  $T = 195^\circ K, \lambda = 1.25 \mu$



[Ref. 7700]

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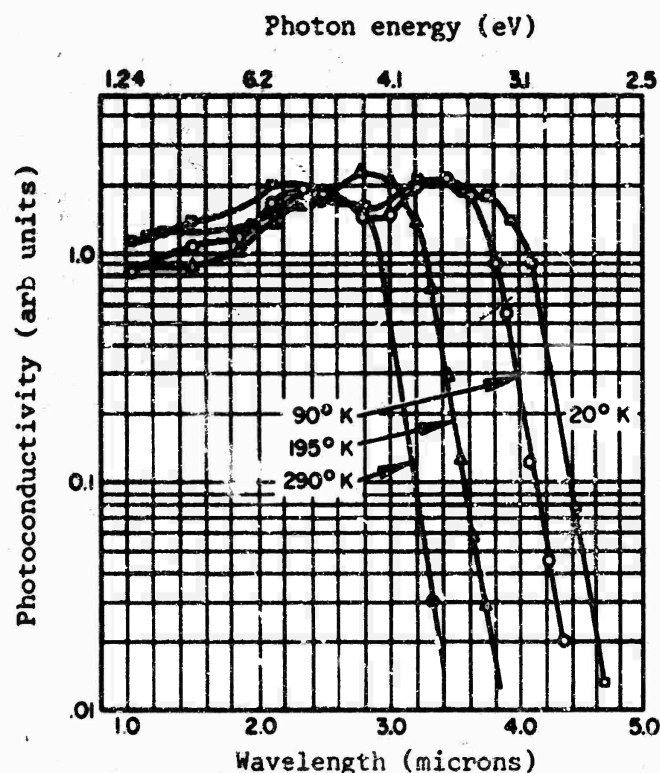


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## LEAD SULFIDE

### PHOTOELECTRONIC PROPERTIES



Spectral sensitivity of lead sulfide films at four temperatures indicates a temperature shift of  $4 \times 10^{-4}$  eV/°K in the long wavelength limit of sensitivity.

Lead sulfide is a semi-conductor with a relatively low concentration of free current carriers at 300°K. The density of carriers potentially available, however, is high and when freed by radiant energy, the lead sulfide becomes photoconductive. In order, therefore, for the material to become photoconductive at a given wavelength, it must absorb at that wavelength. The fall in photosensitivity at long wavelengths arises from the fall in absorption, i.e. the radiation quanta at that wavelength do not have sufficient energy to free photoelectrons. With regard to temperature, since  $E = kT = 1/\lambda$ , rise in temperature always moves the wavelength toward the shorter wavelengths.

[Ref. 149]

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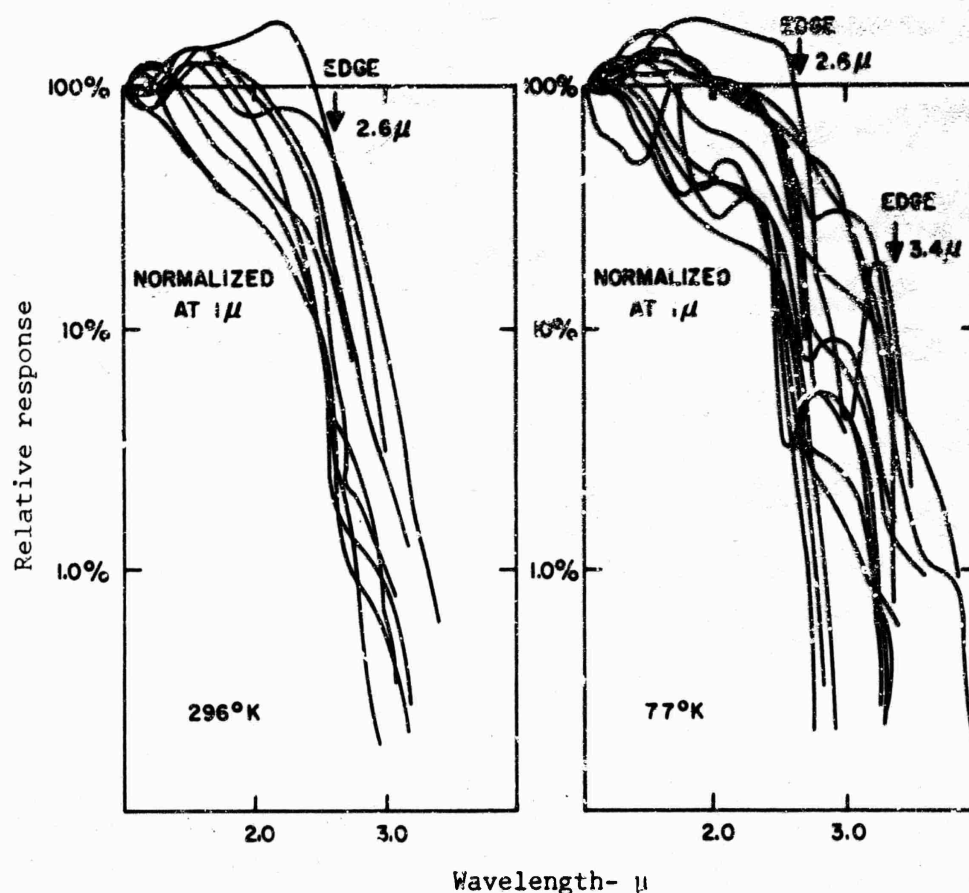


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## LEAD SULFIDE

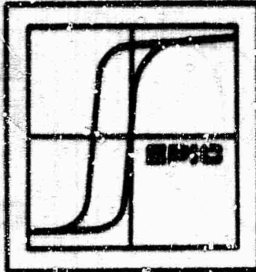
### PHOTOELECTRONIC PROPERTIES



Photoconductive response as a function of wavelength in lead sulfide films. The chemically oxidized type was used, apparently this method yields the most sensitive cells. Data are taken at two temperatures. Irregularities in curves are due partly to optical interference effects resulting from fact that film thickness is similar to wavelength employed.

[Ref. 870]

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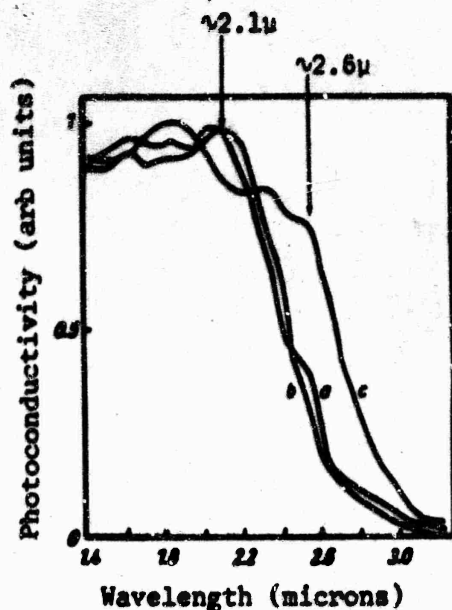


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## LEAD SULFIDE

### PHOTOELECTRONIC PROPERTIES



Photoconductivity as a function of wavelength for three lead sulfide polycrystalline films all 1.3 microns thick and Ag-doped. Grain size is different and the larger the grain, the higher is the long wavelength limit.

Here there is a difference of .5 microns between a and b on the one hand, and c on the other hand.

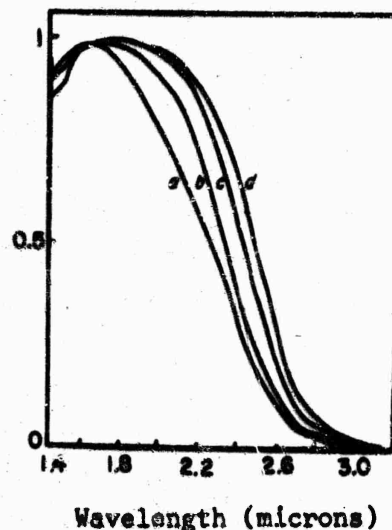
[Ref. 20142]

Same films annealed for 10 minutes in either air, oxygen, hydrogen or a vacuum.

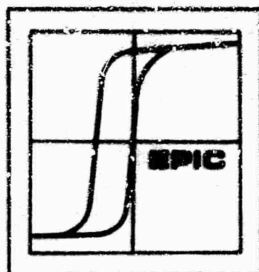
- a = untreated
- b = 100°C
- c = 300°C
- d = 500°C

Heating increases the grain size by recrystallization and therefore shifts the photoconductivity to a longer wavelength limit. There is however a critical value for the grain size and further heating does not increase the photoconductivity.

[Ref. 20142]

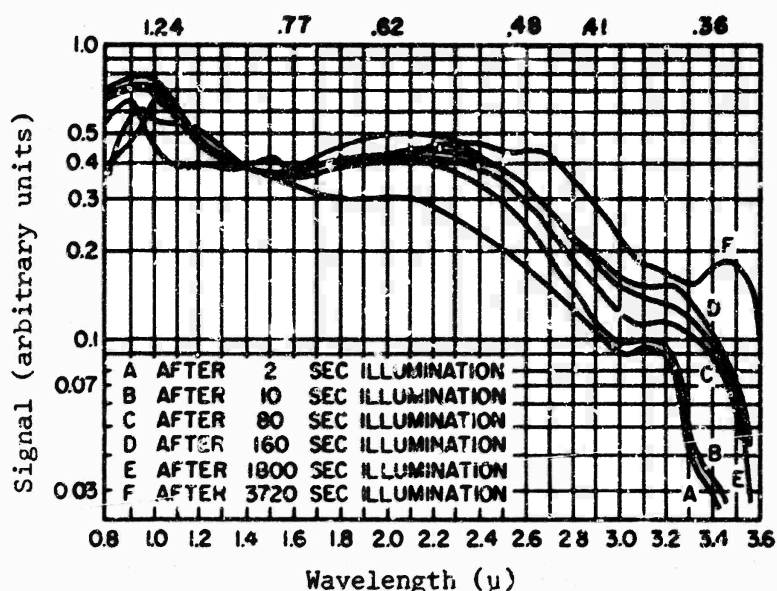






# LEAD SULFIDE

## PHOTOELECTRONIC PROPERTIES



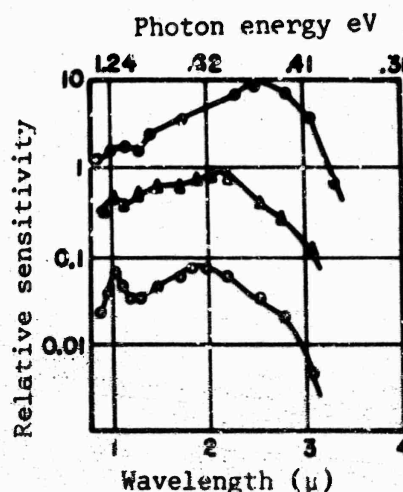
Spectral response for different illumination periods in a lead sulfide film, p-type with excess sulfur. (normalized to 1.4 micron value)

Irregularities in curves are due partly to optical interference effects resulting from fact that film thickness is similar to wavelength employed.

[Ref. 11399]

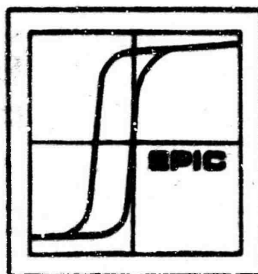
Relative sensitivity as a function of wavelength for lead sulfide evaporated films made photo-sensitive by heating in oxygen. Curves are shown for three temperatures.

- 300°K
- ▲ 195°K
- 90°K



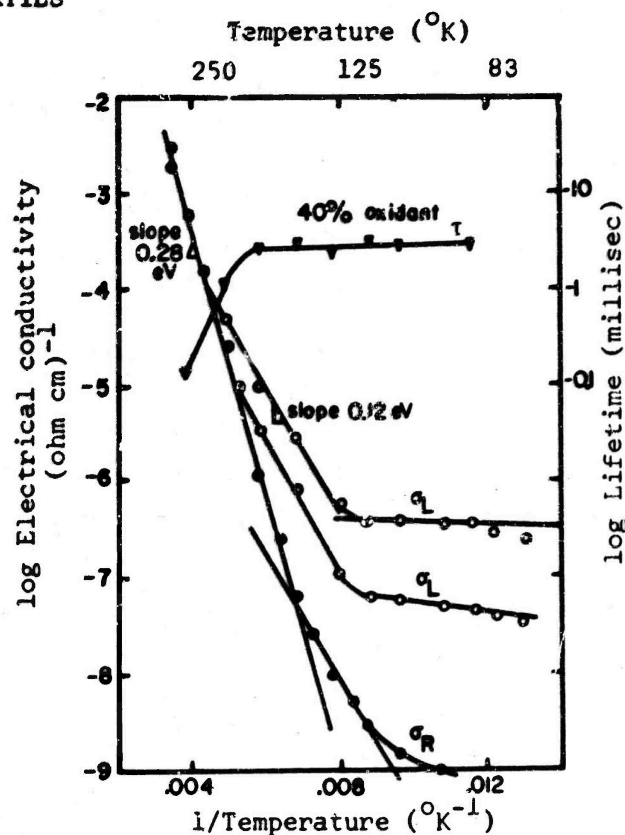
[Ref. 3689]





## LEAD SULFIDE

### PHOTOELECTRONIC PROPERTIES



Photoconductivity and lifetime values as a function of reciprocal temperature for a chemically oxidized polycrystalline lead sulfide film.

$\sigma_L$  is the conductivity at two illumination levels

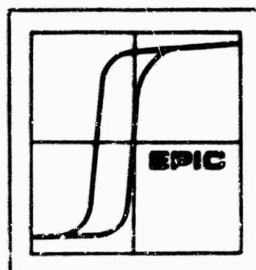
$\sigma_R$  is the dark conductivity

Slope values indicate energy levels for film under varied illumination conduction as a result of an intercrystalline potential barrier structure. Ref. [87C] and [22545] indicate that four conduction mechanisms explain the observed photoconductivity curves:

1. Intrinsic semiconductor over potential barriers.
2. Intrinsic semiconductor by shunt paths.
- 3 and 4 are the same two kinds of impurity semiconductor.

These four mechanisms are variously affected by illumination intensity and other parameters, thus explaining the variety of experimental results.

[Ref. 22545]



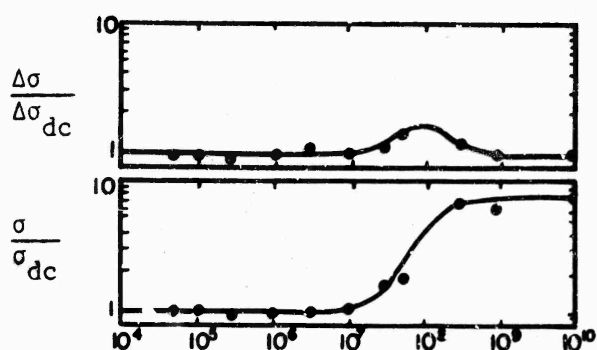
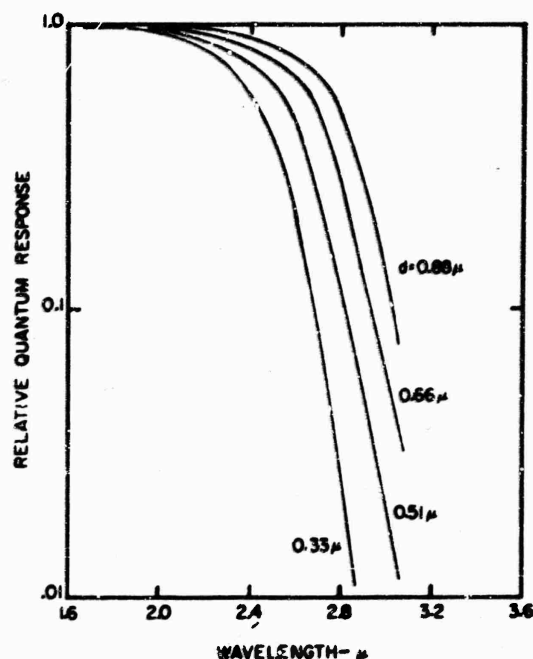
## LEAD SULFIDE

### PHOTOELECTRONIC PROPERTIES

Photosensitivity as a function of wavelength for chemically deposited polycrystalline, lead sulfide films of the given thickness at 300°K. The response is normalized at 1.66 microns. With increasing thickness, the spectral sensitivity of the film is shifted toward longer wavelengths primarily because of decreased absorption. (See page 74)

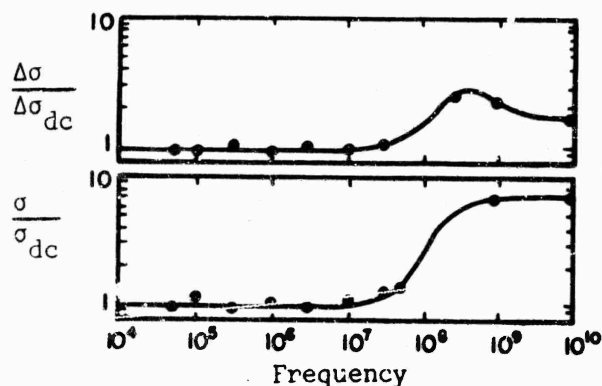
$d$  = film thickness

[Ref. 490]



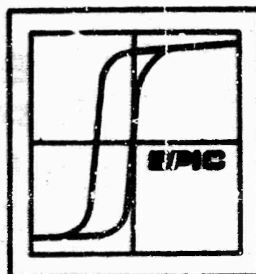
A<sub>1</sub>

Photoconductivity and dark conductivity as a function of frequency for two highly sensitive lead sulfide films. The values are normalized by dc measurements. Data taken at 300°K. Sharp rise in conductivity at approximately 100 Mc indicates thin, high resistivity barriers.



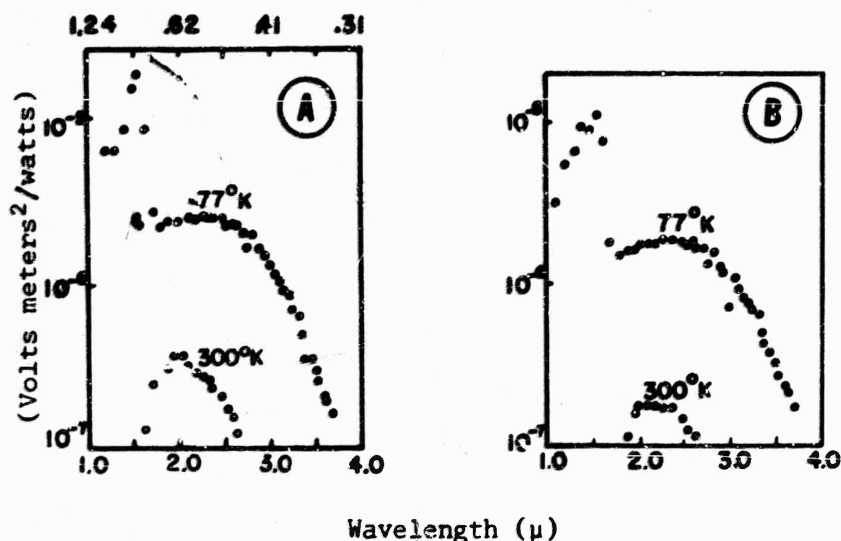
A<sub>2</sub>

[Ref. 284]



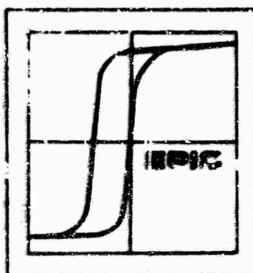
## LEAD SULFIDE

### PHOTOELECTRONIC PROPERTIES



Photovoltage as a function of wavelength for a single crystal lead sulfide film at 77°K and 300°K. The film is grown from a chemical solution, epitaxially, on a germanium substrate at 300°K. In (A) the film is (100) oriented and in (B) it is (111) oriented. The orientation and the 5.97 Å lattice spacing which is the bulk lead sulfide value, is confirmed by diffractometer measurements. The photovoltage is normalized by means of incident illumination volts/(watts/meter<sup>2</sup>). The data has been used to calculate lifetime of excess carriers. At 77°K and 1.55 microns, the lifetime is calculated to be 25 μsec, at 3 microns,  $\tau = 17.5 \mu\text{sec}$ . [Ref. 23389]

The wavelength of the light must approach the germanium edge at about .73 eV (1.7 μ) for the light to penetrate the germanium substrate before being absorbed. This reduces the effect of both surface and bulk recombination and the photovoltage rises. When an appreciable fraction of the light penetrates the entire substrate, it can then penetrate the sulfide film and generate some carriers. There follows a decline in the photovoltage because these latter carriers do not contribute as much to the signal as those generated in the germanium. Beyond the germanium edge, the carriers are generated in the sulfide and the photovoltage is fairly constant until the lead sulfide absorption edge is attained and the signal falls. Increased temperature serves to cut down the spectral sensitivity by increasing recombination of charge carriers.



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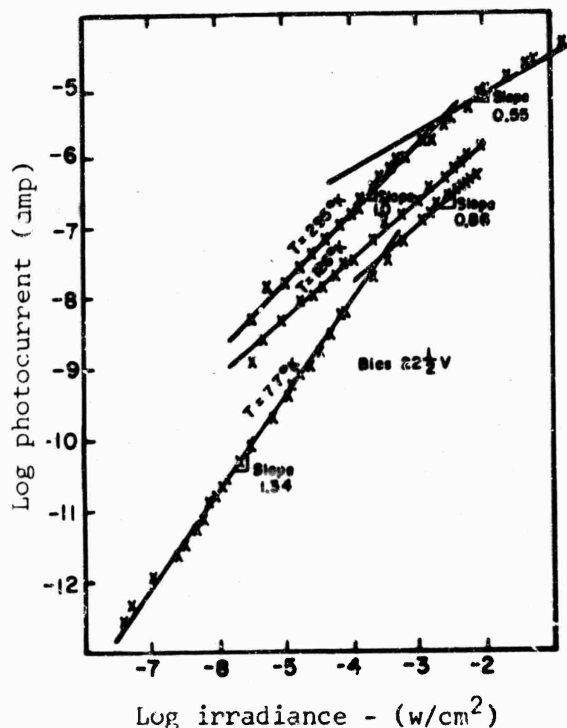
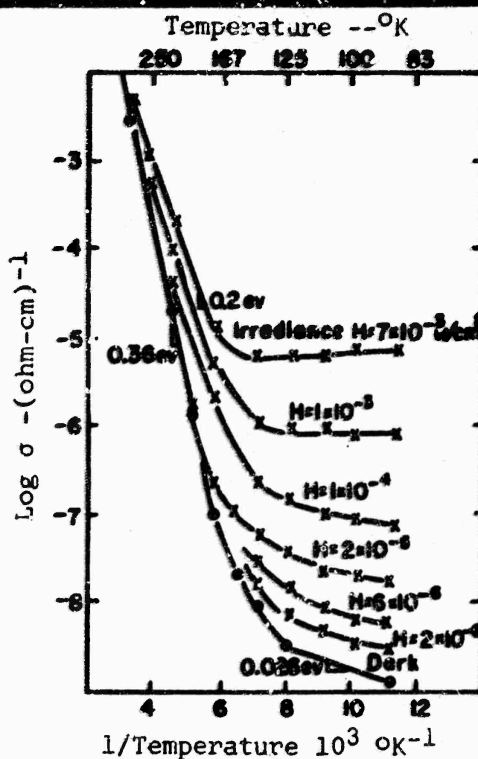
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LEAD SULFIDE

PHOTOELECTRONIC PROPERTIES

Log photoconductivity as a function of reciprocal temperature for a chemically oxidized lead sulfide film at a variety of radiation intensities. This film has a maximum energy gap (0.36 eV).

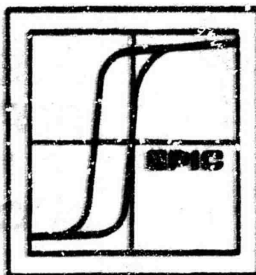
[Ref. 870]



Log photocurrent as a function of log radiation at 22.5 volts and three film temperatures for a lead sulfide film similar to the one above. The variation may deviate more or less from the linear at low temperatures, but at higher temperatures, slopes lie fairly close to 1.0, and above  $125^\circ\text{K}$  the slope is never more than 1.

[Ref. 870]





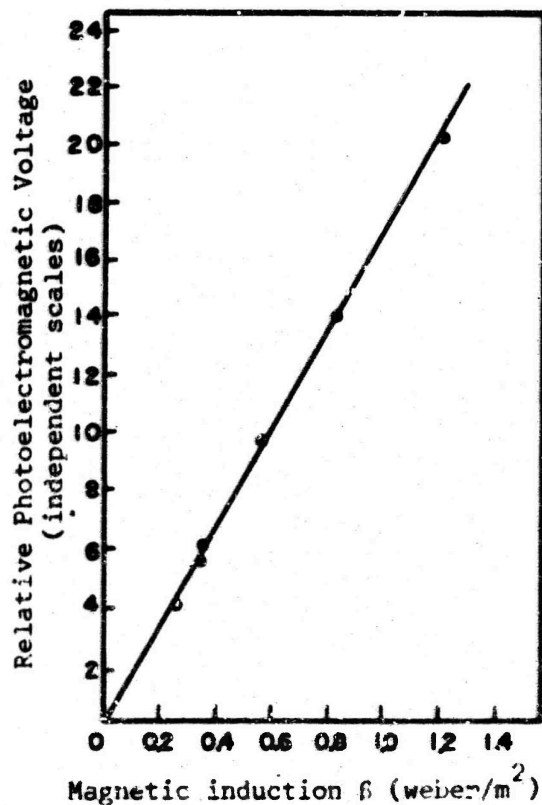
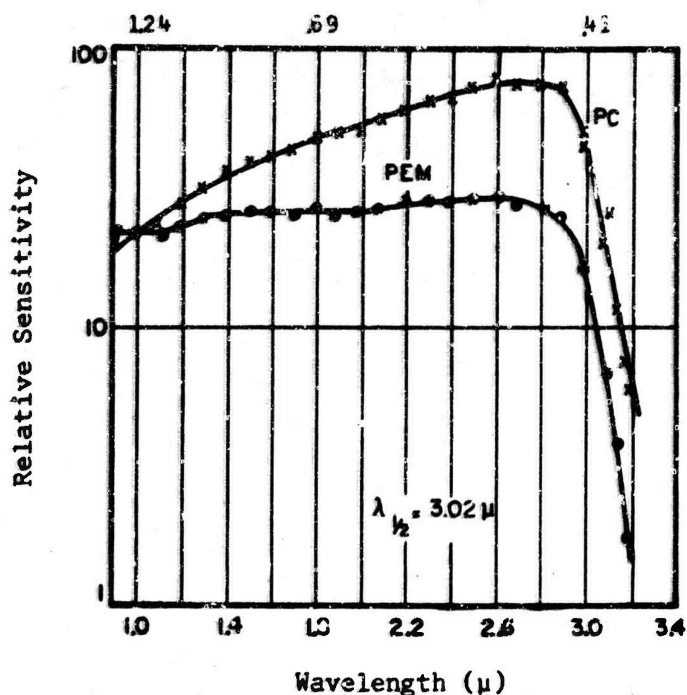
## LEAD SULFIDE

### PHOTOELECTRONIC PROPERTIES

Photosensitivity as a function of wavelength for single crystal lead sulfide, (100) cleaved. The decrease in sensitivity is approximately linear. 50% maximum sensitivity is found at 3.02 microns. Sensitivity drops sharply at .411 eV, the photoconductivity energy gap.

$$\lambda_{\frac{1}{2}} = 3.02 \text{ microns} = .41 \text{ eV}$$

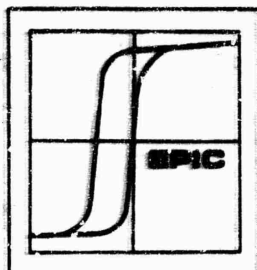
[Ref. 2835]



Photoelectromagnetic voltage as a function of magnetic induction in natural single crystal lead sulfide, (100) cleavage plane,  $\rho = 0.23 \Omega \text{ cm}$ .

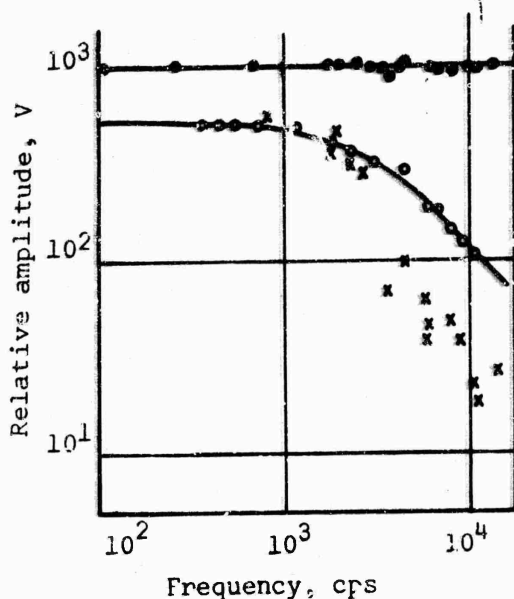
[Ref. 2835]





# LEAD SULFIDE

## PHOTOELECTRONIC PROPERTIES



Photovoltaic, photoconductive and photoelectromagnetic response to frequency in polycrystalline lead sulfide films 60 microns thick at 300°K.

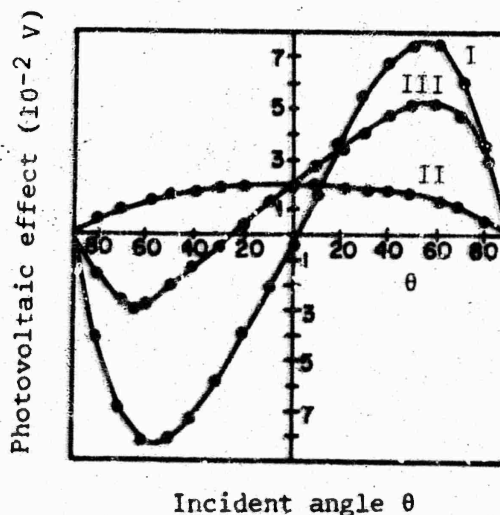
Photovoltaic response shows no time constant effects. But photoelectromagnetic is even more strongly affected by frequency than photoconductivity. Evidently traps hold the minority carriers and surface recombination is delayed. This mechanism provides the film sensitivity or photoconductivity.

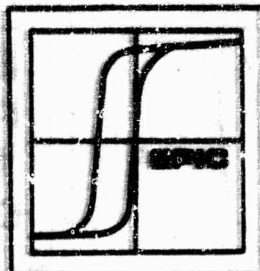
- Photovoltaic
- Photoconductive
- x Photoelectromagnetic at 9.6 kGauss

[Ref. 7700]

Photovoltage emf as a function of incident angle ( $\theta$ ) at 300°K for polycrystalline lead sulfide film annealed in air at 500-620°C (I). These induced voltages are modified in curve II by p-n-type junction emf. Curve III is a summation of I and II.

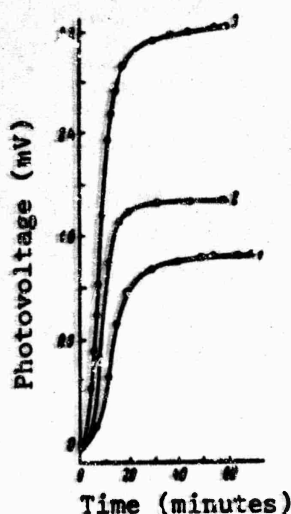
[Ref. 3533]





## LEAD SULFIDE

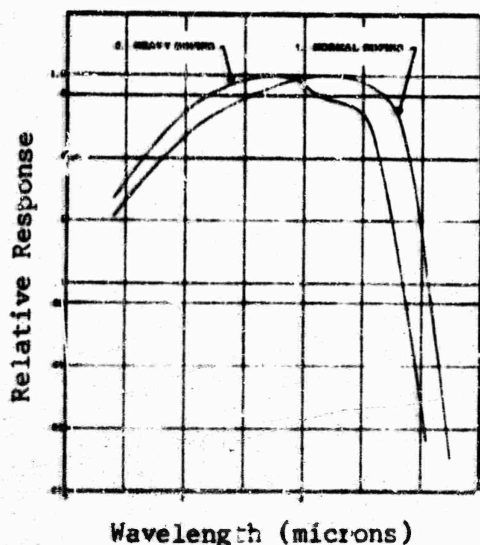
### PHOTOELECTRONIC PROPERTIES



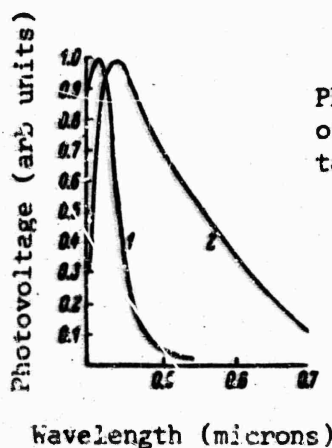
Increase in photovoltage method increased oxygen absorption, in single crystal lead sulfide epitaxial films. The absorption of oxygen at 300°K, accompanied by considerable changes in the film resistivity, creates a surface barrier across which a surface photo-emf is possible on illumination. However, as a result of high surface recombination, this voltage is small or non-existent. On the other hand, the low temperature absorption of oxygen, unaccompanied by free electron capture, alters the surface recombination and increases the surface photovoltage. Measurements of photovoltage at 77°K.

- 1) .018 mm Hg of oxygen pressure
- 2) .03
- 3) .05

[Ref. 25677]



Relative spectral response of PbS detectors at 298°K with normal and with heavy oxide doping. [Ref. 22736]



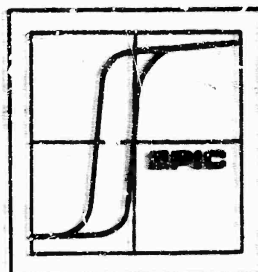
Photovoltage as a function of wavelength in polycrystalline films at 90°K.

1. Lead oxide
2. Lead sulfide

[Ref. 2548]

Highly sensitive lead sulfide cells require an optimum amount of the oxide possible. Heavy doping of these lead sulfide films, moves the spectral peak at 298°K continuously, from 2.3 to 1.5 microns, by shifting the energy gap from the 0.4 eV of lead sulfide to the 2.6 eV of lead oxide. Comparison of the lead oxide and the lead sulfide photo-emf at 90°K is shown for polycrystalline films in [Ref. 2548]

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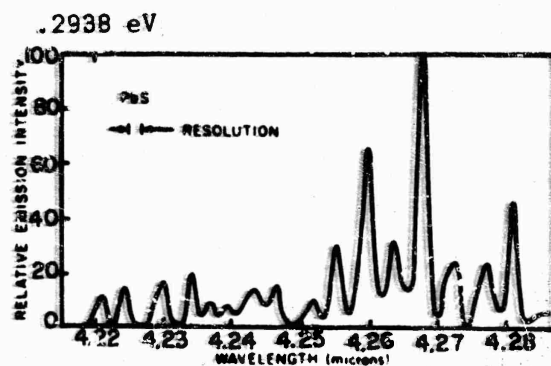


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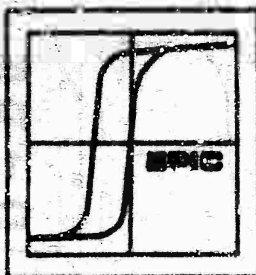
PHOTON ELECTROLUMINESCENCE



Photon electroluminescence intensity  $\sim$  wavelength in an n-type lead sulfide laser,  $n = 2.5 \times 10^{18} \text{ cm}^{-3}$ , cleaved from a synthetic single crystal (100) plane. Electron beam energy is 50 keV, temperature is 4.2°K. Average wavelength separation between modes is 40 Å.

$\mu$	eV
4.22	.2938
4.23	.2931
4.24	.2924
4.25	.2917
4.26	.2910
4.27	.2903
4.28	.2897

[Ref. 22863]



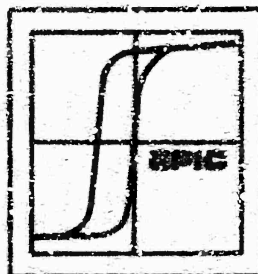
**LEAD SULFIDE**

**PHOTON EMISSIVITY**

Increased coating weight decreases the reflectance at both long and short wavelengths and increases the spectral emittance which is more strongly affected by film thickness than is the absorption. This increase in emittance sets the optimum value of coating thickness at a point where further increase in solar absorption is disadvantageous because of large emissivity increase.

<u>Spectral Emissivity</u>	<u>Coating Weight mg/cm<sup>2</sup></u>	<u>Film Character</u>	<u>Wavelength</u>	<u>Temp.</u>	<u>Ref.</u>
0.05	0.68	aluminum substrate, solid film comprising dendritic lead sulfide of 0.1 micron branch diameter.	715 $\mu$	520°K	22735
0.12	0.20				
0.16	0.46				
0.19	0.68				
0.30	1.26				
0.51	2.30				
0.60	0.68	same aluminum substrate with solid film comprising cubic lead sulfide crystals with particle size from 0.2 to 1.1 microns			
0.75	4.20	"			





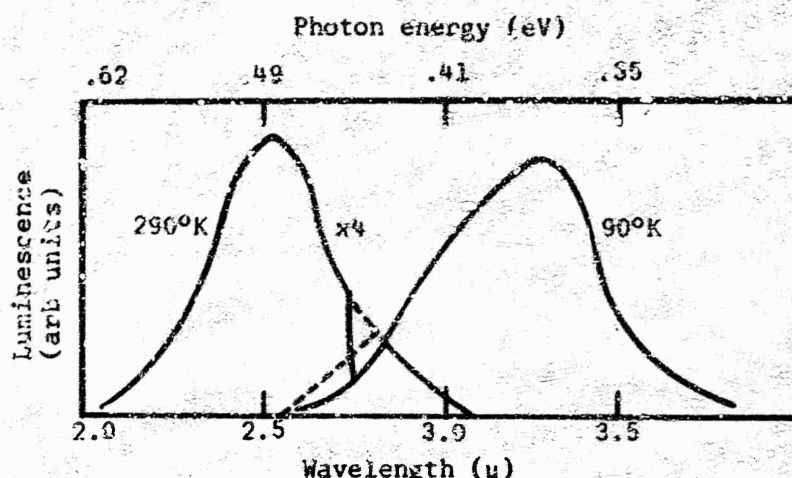
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# LEAD SULFIDE

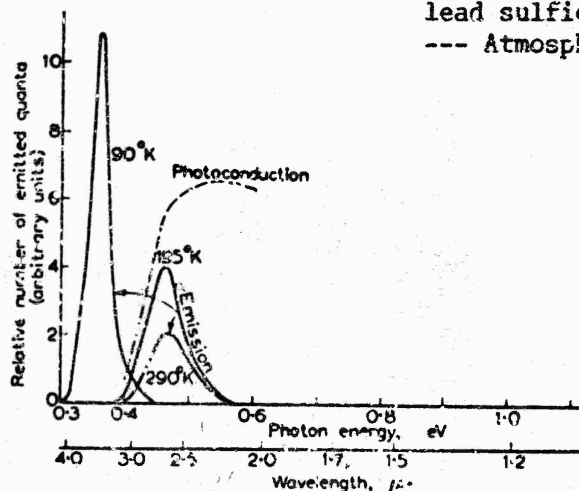
## PHOTON LUMINESCENCE

- a - 290°K (x4)
- b - 90°K
- Atmospheric Absorption

[Ref. 22690]



Photon luminescence as a function of wavelength in lead sulfide films at two temperatures.  
--- Atmospheric Absorption

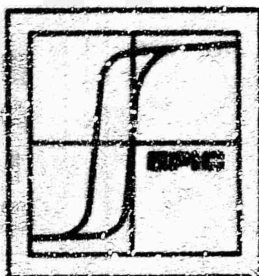


Photon emission and photoconductivity as a function of wavelength in lead sulfide films at three temperatures. One photon luminescence band appears where photoconductivity is falling off with increased wavelength and this band also moves to longer wavelengths with a temperature decrease. The emission apparently arises from electron transitions between levels close to the bottom of the conduction band and the top of the valence band. Charge carriers are trapped before the transitions take place so that the emission is due to recombination.

[Ref. 22690] shows the wavelength shift with temperature in detail.

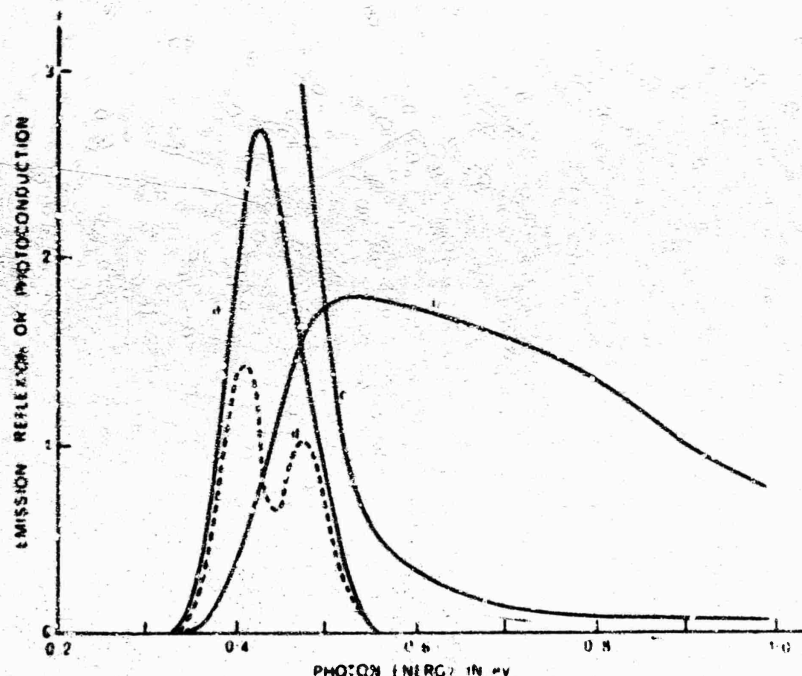
[Ref. 9749]





# LEAD SULFIDE

## PHOTON LUMINESCENCE



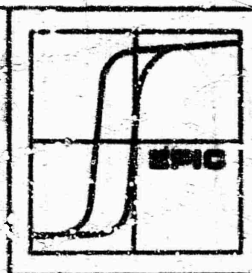
Excitation, emission and photoconductive response spectra for lead sulfide samples at 290°K.

Emission spectra as a function of photon energy in an evaporated, post-oxidized lead sulfide film at 290°K.

- a. Photon luminescence
- b. Photoconductivity
- c. Diffuse reflection
- d. Photon luminescence in a poorly photoconductive film.

The photoconductivity response spectrum indicates that this is a highly efficient film and the peak locations are shifted toward a longer wavelength. (d), the emission spectrum for a poorly photoconductive cell has a peak at about one-half the production at the same wavelength as (a), indicating either two different recombination centers or more than one transition energy at the same center.

[Ref. 22971]



# LEAD SULFIDE

## PIEZOELECTRIC PROPERTIES

Piezoresistance Coefficients ( $10^{-12}$  cm<sup>2</sup>/dyne)

$\pi_{11}$	$\frac{1}{2}(\pi_{11} + \pi_{12} + \pi_{44})$	$\pi_{11} + 2\pi_{12}$	Carrier Conc. $n_0$ (cm <sup>-3</sup> )	Temp. °K
+7.7±0.2	-7.4±0.2	+35.0±0.8	10 <sup>17</sup>	293
+8.8±0.5	-6.1±0.8	+34.0±5.8	10 <sup>16</sup>	293
-3.3±0.8	-49.6±1.8	-2.3±1.6	10 <sup>17</sup>	90
-9.0±0.2	-52.5±6.5	-8.4±0.5	10 <sup>16</sup>	90
—	—	-9.2±0.3	10 <sup>17</sup>	77
—	—	-18.8±0.4	10 <sup>16</sup>	77
-30.2±0.3	-111.6±3.6	—	10 <sup>17</sup>	20
-37.8±2.0	-109.8±2.6	—	10 <sup>16</sup>	20
-16.5±1.2	-140.1±0.3	-52.5±3.0	10 <sup>17</sup>	4.2
-20.2±0.2	—	—	10 <sup>16</sup>	4.2

Measurements made on natural galena samples, single crystal, n-type, (100) and (110) oriented.

$\pi_{11}$  = Current and stress applied parallel to (100) crystallographic plane.

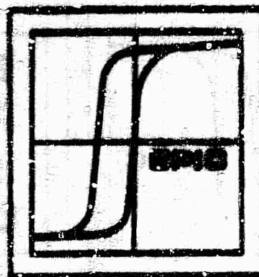
$\frac{1}{2}(\pi_{11} + \pi_{12} + \pi_{44})$  = Current and stress applied parallel to (110) crystallographic plane.

Change in resistivity with pressure yields the third measurement necessary to separate the coefficients.

Piezoresistance measurements give strong indication that the conduction band minima are located along the (111) axes in k-space.

[Ref. 28751]

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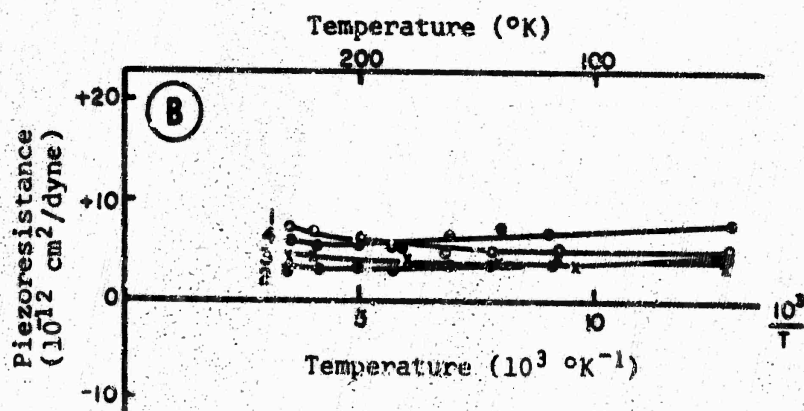
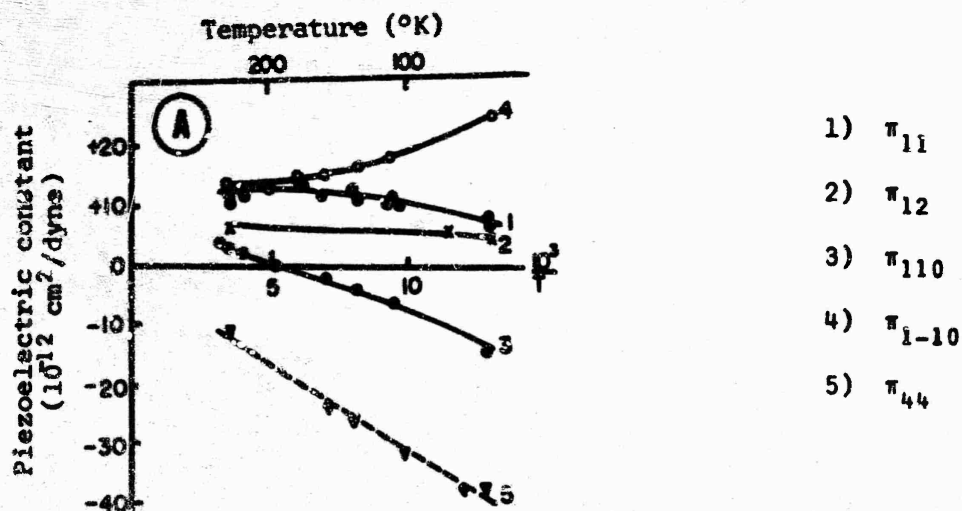


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# LEAD SULFIDE

## PIEZOELECTRIC PROPERTIES ( $\pi$ )



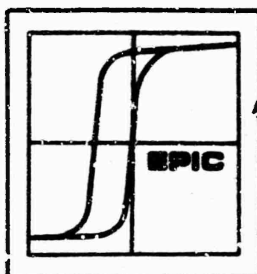
Piezoelectric constant as a function of reciprocal temperature in n-type single crystal lead sulfide at 78 - 293°K.

A, electron carrier concentration  $n_n = 1 - 3 \times 10^{18} \text{ cm}^{-3}$

B, electron carrier concentration  $n_n = 6 - 9 \times 10^{19} \text{ cm}^{-3}$

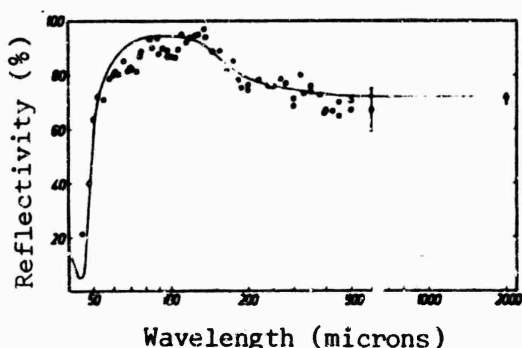
[Ref. 7729]





# LEAD SULFIDE

## REFLECTION COEFFICIENT

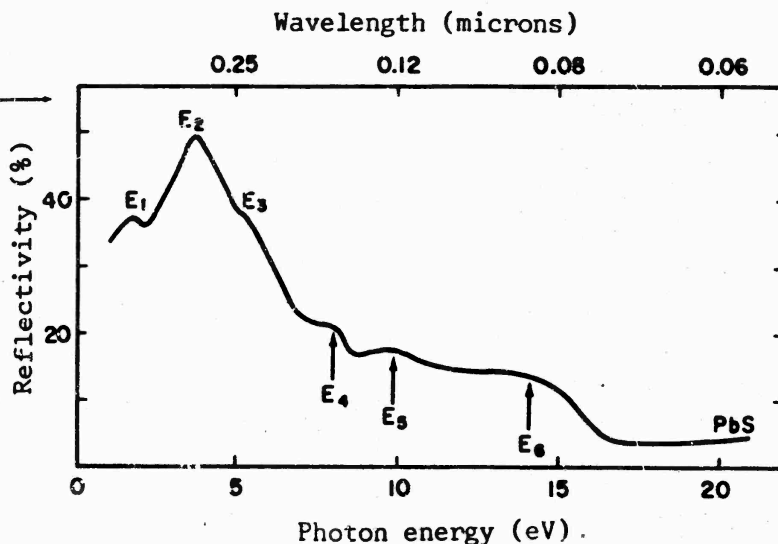
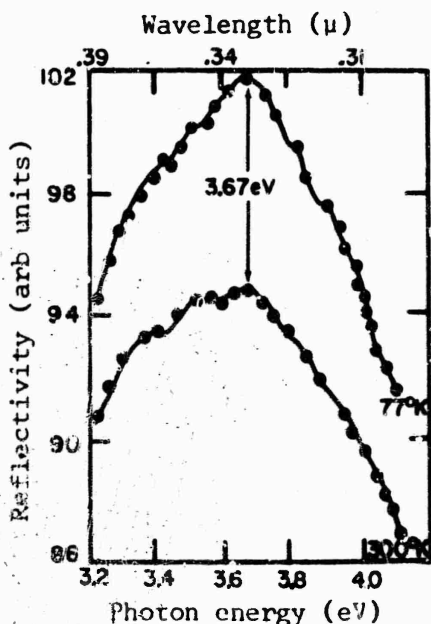


Reflectivity as a function of wavelength in the far infrared for a natural lead sulfide single crystal,  $n = 10^{16}\text{cm}^{-3}$ . The curve has the typical shape of a lattice reflection spectrum. The point at 2000 microns was taken on a sample with  $10^{17}\text{cm}^{-3}$ .

[Ref. 26151]

Reflectivity as a function of photon energy for single crystal lead sulfide. Measurements below 6 eV were made on cleaved (100) surfaces. Above that point in the vacuum UV, data was taken on epitaxial films. All measurements at 297°K.

[Ref. 14189]



The  $E_2$  reflectivity peak in single crystal lead sulfide, (100) cleavage planes, at 77°K and 300°K. The curves show fine structure and temperature shift. Latter is  $\sim .5 \times 10^{-4} \text{ eV/}^\circ\text{K}$ .

[Ref. 14189]





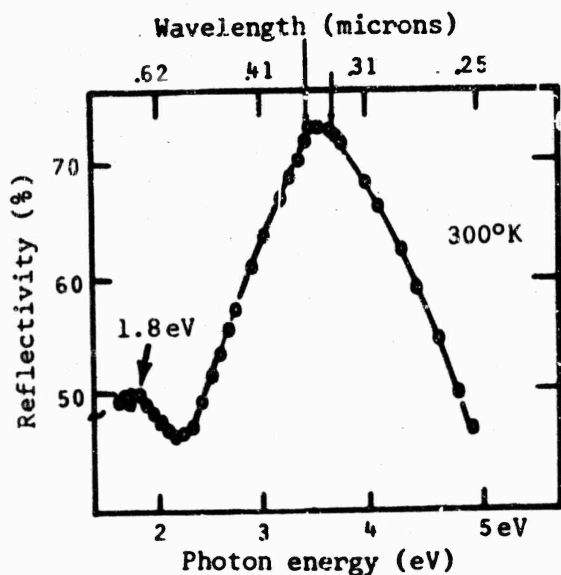
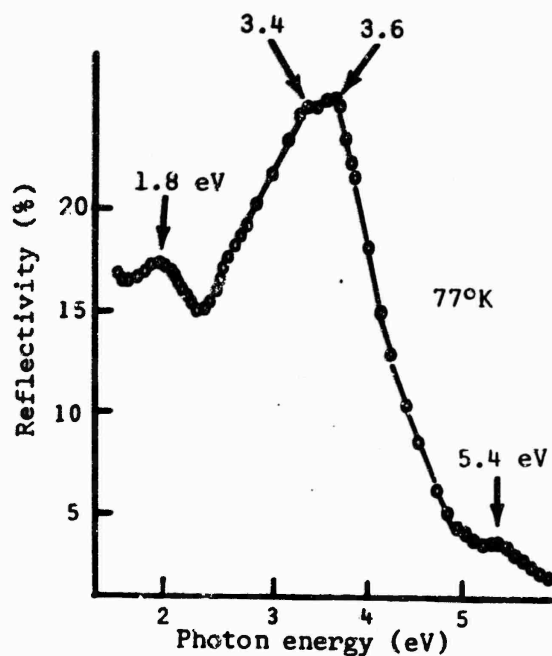
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## LEAD SULFIDE

### REFLECTION COEFFICIENT

Reflectivity as a function of photon energy for single crystal lead sulfide, cleaved (100) surface, at 77°K.

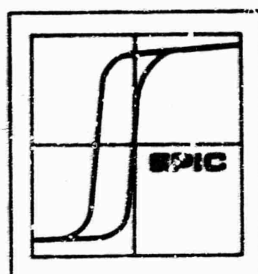
Main peak at 3.6 eV has a doublet structure, due to spin orbit splitting of valence band. Split is about 0.2 eV. There are maxima at 5.4 eV and 1.8 eV.



Reflectivity as a function of photon energy for single crystal lead sulfide, cleaved (100) surfaces, at 300°K.

The same doublet structure is seen at 3.6 eV but at this temperature no observations are possible above 5 eV due to absorption.

[Ref. 14197]



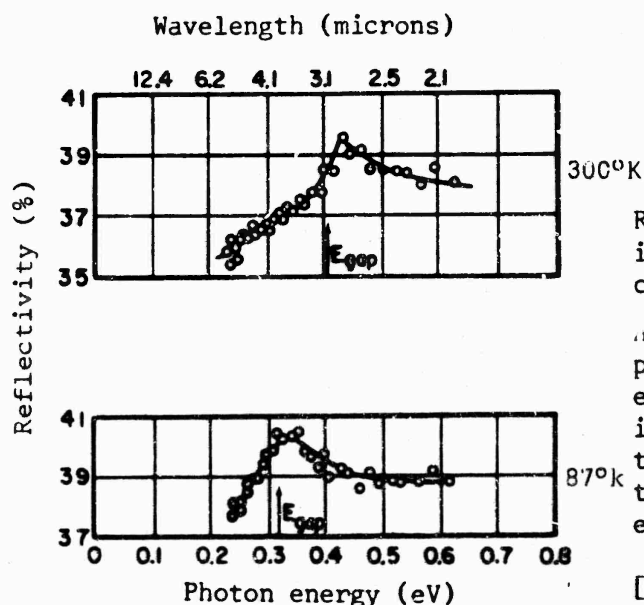
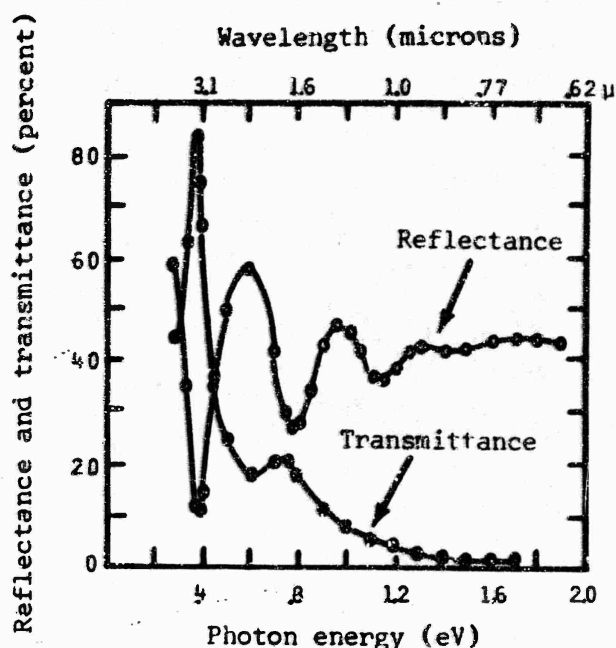
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# LEAD SULFIDE

## REFLECTION COEFFICIENT

Reflectance and transmittance as a function of photon energy of a 0.37 micron thick lead sulfide single crystal epitaxial film, at 300°K.

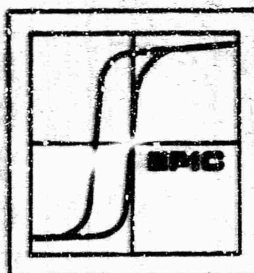
[Ref. 17982]



Reflectivity as a function of photon energy in n-type single crystal lead sulfide (100) cleavage planes at 300°K and 87°K.

At 300°K, deviation of the reflectivity peak from the intrinsic single crystal energy gap is a result of dispersion and is at a considerable higher energy than the absorption edge. At low temperature, the peak varies very slightly from the energy gap.

[Ref. 13718]

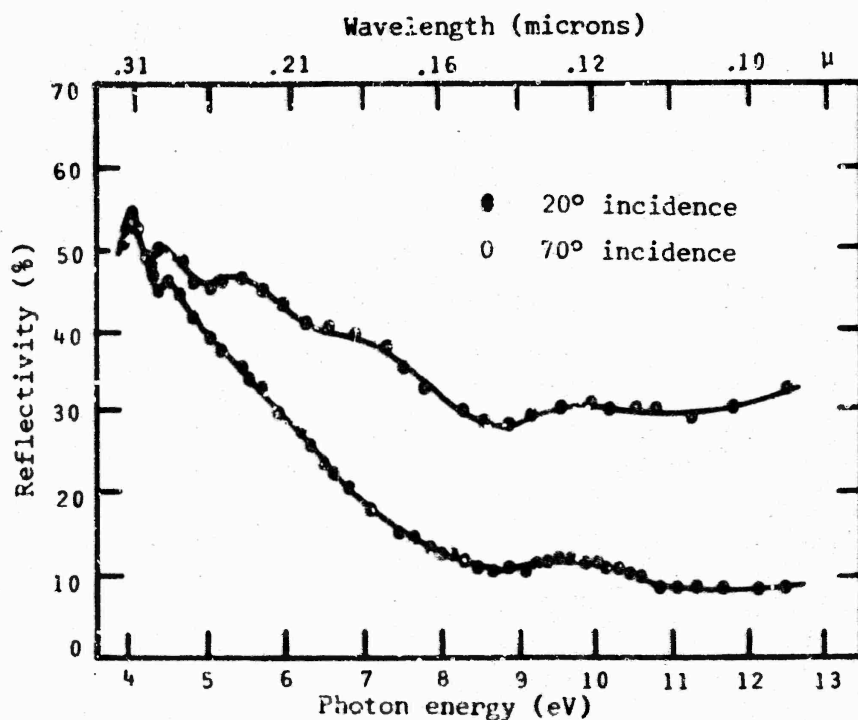
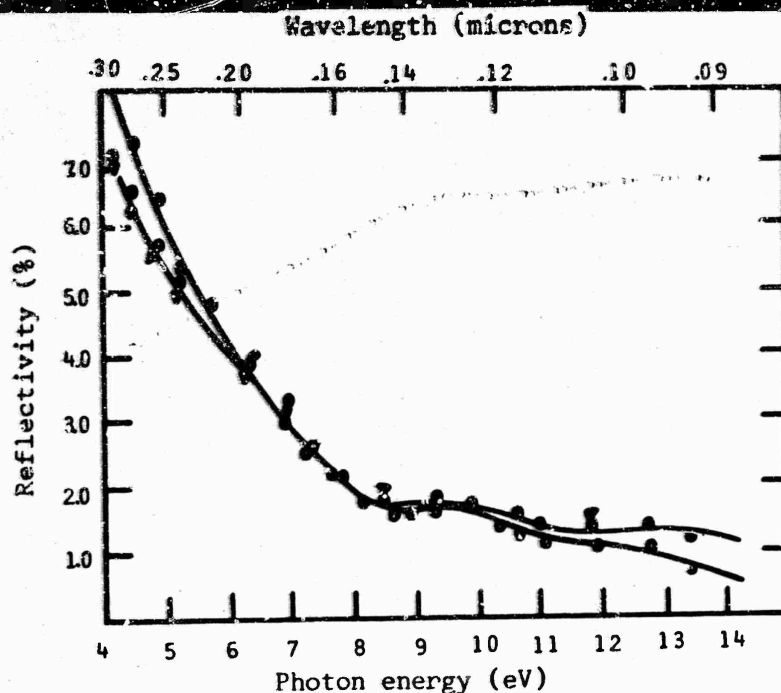


# **LEAD SULFIDE**

## **REFLECTION COEFFICIENT**

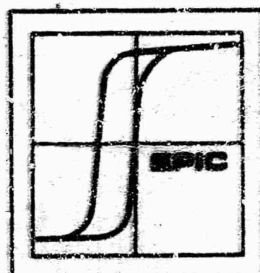
Reflectivity as a function of photon energy for three polycrystalline chemically deposited films of lead sulfide. Incidence of illumination is  $20^\circ$  to surface. High crystallite size reduces reflectivity. (Films are not further identified).

[Ref. 16824]



Reflectivity as a function of photon energy in natural galena crystals, (100) cleavage planes. The curves show increase in the UV with decrease in angle of incidence of illumination.

[Ref. 13554]



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# LEAD SULFIDE

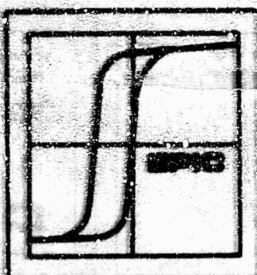
## REFRACTIVE INDEX (n)

Value	Sample	Wavelength	Temp.	Ref.
4.10 ± 0.06	single crystal, natural and synthetic, (100) cleavage plane	3 μ	300°K	3453
4.19 ± 0.06	single crystal, synthetic, (100) cleavage plane	6 μ	20°C	3452
$d_n/d_t = -(5.5 \pm 1.5) \times 10^{-4} \text{ } ^\circ\text{C}^{-1}$		6 μ	20 - 315°C	3452

n	Wavelength (microns)		Temp.	Ref.
4.00	5.1	lead sulfide single crystal	300 °K	26201
4.00	5.5	epitaxial film		
3.98	5.9	thickness = 10.3 μ		
3.99	6.3	n-type		
4.00	6.9	$n = 9 \times 10^{17} \text{ cm}^{-3}$		
4.00	7.5			
4.00	8.2			
3.92	9.1			
4.04	10.4			
3.99	11.7			
4.00	3.4	second sample	300 °K	26201
3.97	3.8	thickness = 3.8 μ		
3.90	4.2	p-type		
3.88	4.9	$n = 6 \times 10^{17} \text{ cm}^{-3}$		
3.82	5.8			
3.77	7.1			
3.67	9.3			
3.43	13.0			

Refractive index as a function of wavelength for two thicknesses of epitaxial film obtained by vacuum evaporation on halite crystals. At 10 microns, there is practically no dispersion of the refractive index whereas in the thinner film, the index decreased with increased wavelength, i.e. dispersion was normal





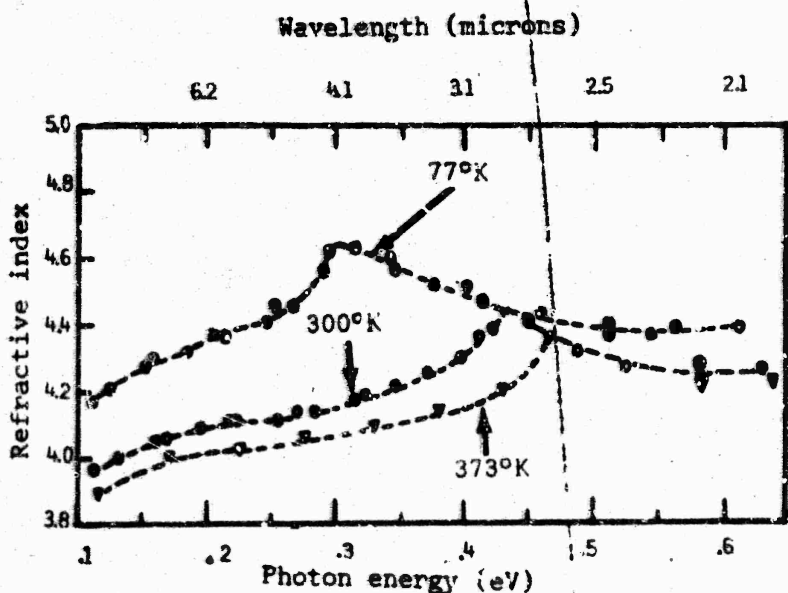
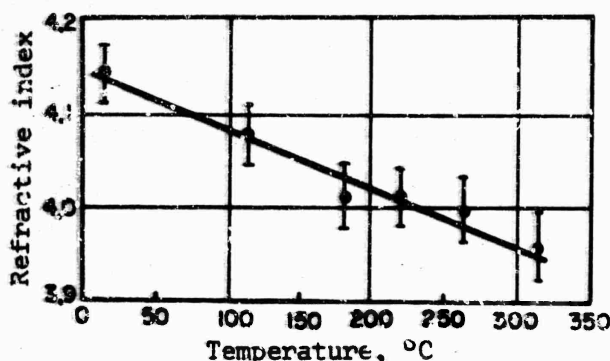
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# LEAD SULFIDE

## REFRACTIVE INDEX (n)

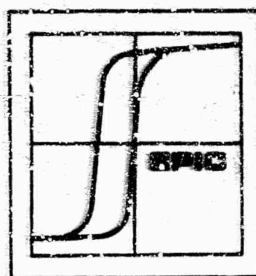
Refractive index as a function of temperature for single crystal synthetic lead sulfide (100) cleavage planes.

[Ref. 3452]



Refractive index as a function of photon energy for single crystal epitaxial films of lead sulfide at three temperatures. Films of varied thickness from 0.2-8 $\mu$  were used. The peak on each curve is associated with the rapid change in absorption coefficient at the direct optical transition. As the temperature decreases the energy gap decreases.

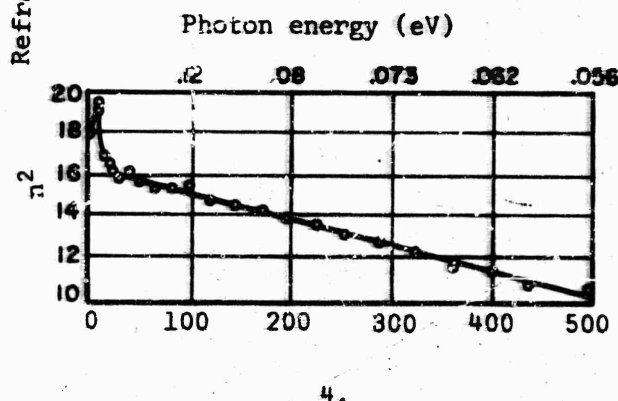
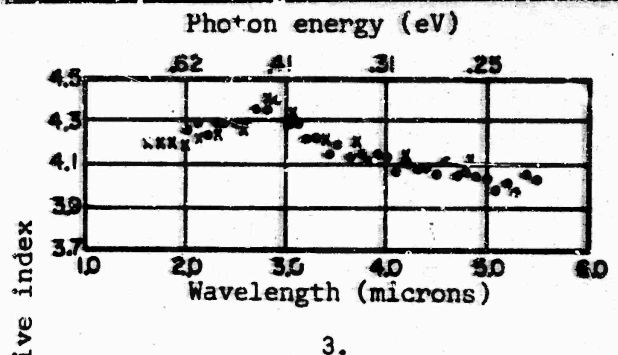
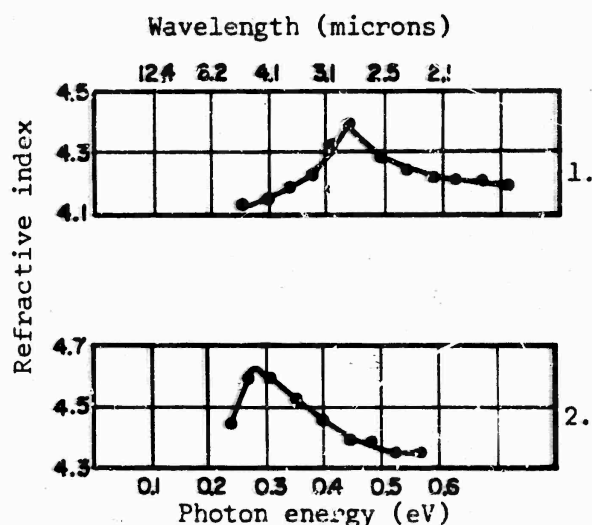
[Ref. 22079]



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# LEAD SULFIDE

## REFRACTIVE INDEX



Refractive index as a function of photon energy for single crystal lead sulfide.

- 1) Epitaxial film. Data obtained from interference fringes produced by reflection at 300°K.
- 2) Epitaxial films - data at 91°K.
- 3) Data from (100) cleavage planes in single crystals at 300°K compared with film data.
- 4) Index and wavelength squared for cleavage planes at 300°K. The peak at  $\lambda^2 = 8\mu^2$  shows an increase in the extinction coefficient at the absorption edge.

At room temperature, the peak in the refractive index occurs at slightly higher energy than the energy gap. At low temperature the peak moves to smaller energy value but differs significantly from the gap.

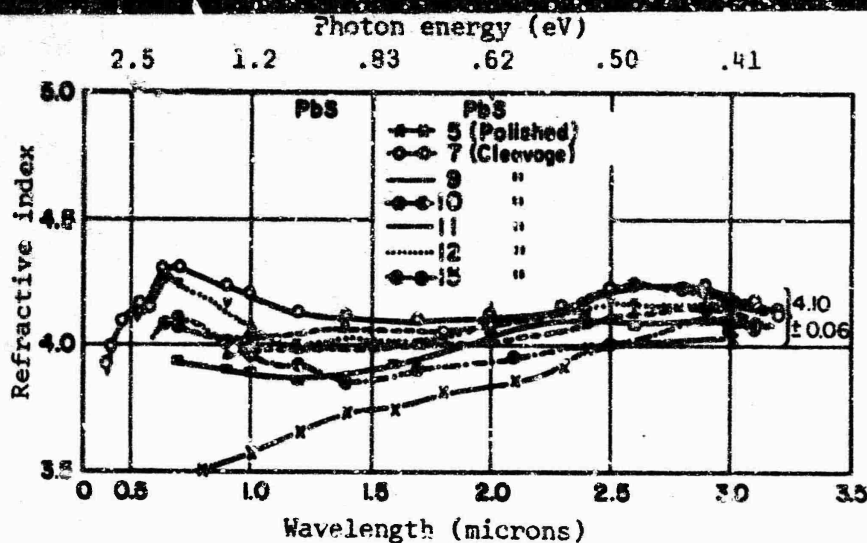
[Ref. 13718]

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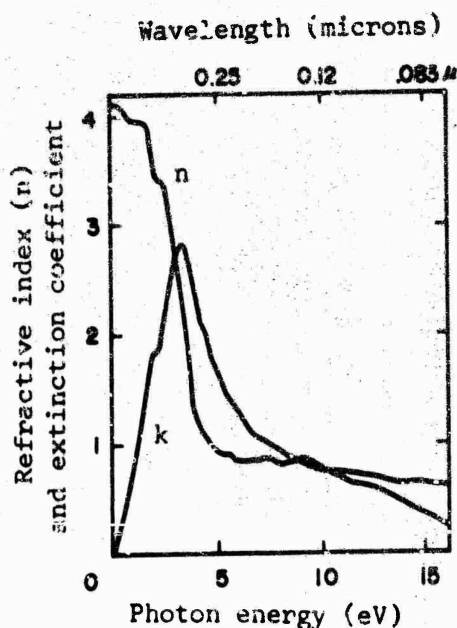
## REFRACTIVE INDEX

Refractive index as a function  
of wavelength for single crystal  
lead sulfide. Samples 9  
and 11 are synthetic.  
The others are  
natural galena.  
Data taken at  
300°K.



[Ref. 3453]

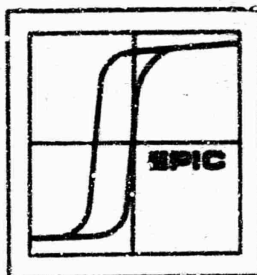
<u>No.</u>	<u>Type</u>	<u>n, 10<sup>17</sup> cm<sup>-3</sup></u>
5	p	600
7	n	4.5
9	p	200
10	p	13
11	p	15
12	n	70
15	n	0.6



Refractive index (n) and extinction coefficient (k) as a function of photon energy at 297°K for single crystal lead sulfide. Below 6 eV measurements are made on (100) cleavage planes. Above 6 eV epitaxial films are used. Curves are calculated from reflectivity data.

[Ref. 14189]

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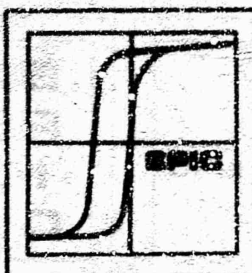
THERMAL CONDUCTIVITY (k)

<u>Value (watts/cm deg)</u>	<u>Temperature</u>	<u>Ref.</u>
0.008	300°K	7359
0.0067		*

- \* IOFFE, A.V. and IOFFE, A.P. Study of the Correlation of Thermal Conductivity of Semiconductors with Free Electrons. ZHURNAL TEKHICHESKOI FIZIKI, v. 24, no. 10, 1954. p. 1910-1911.

Thermophysical property data is compiled by the Thermophysical Properties Research Center and data, other than that incidentally compiled here, may be available from them. TPRC is located in Lafayette, Indiana.





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## LEAD SULFIDE

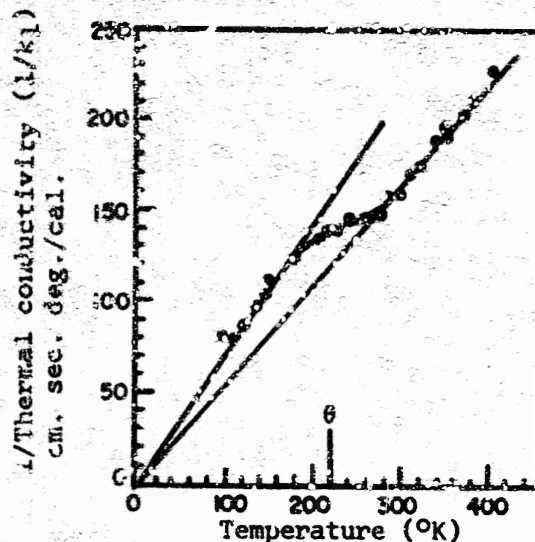
### THERMAL CONDUCTIVITY

Reciprocal lattice thermal conductivity as a function of temperature for single crystal, natural lead sulfide.  $n$  varies from  $10^{16}$ - $10^{18}$   $\text{cm}^{-3}$ .  $\theta$  is the Debye temperature.

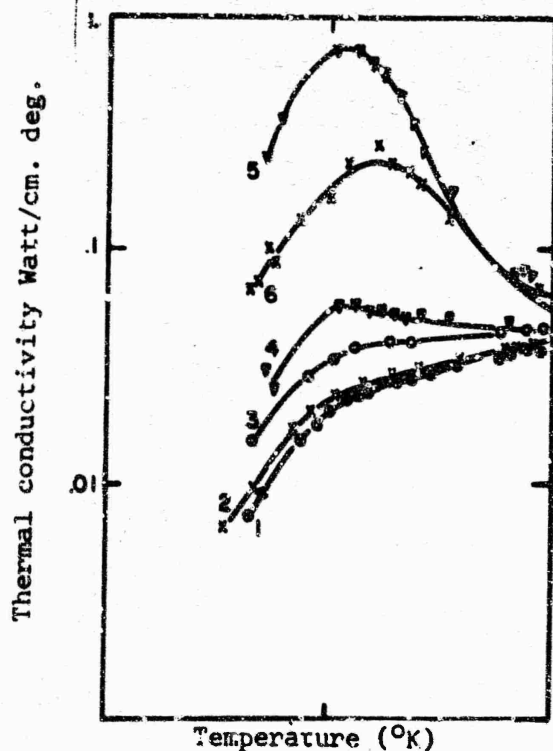
Some scattered points on the curve are taken from [Ref. 285]

$w/\text{cm } ^\circ\text{K}$	$1/k_1$	$k_1$
.017	250	.004
.021	200	.005
.038	150	.006
.042	100	.01
.084	50	.02

$k_1$  = lattice thermal conductivity.



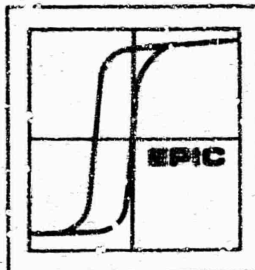
[Ref. 22574]



Thermal conductivity as a function of temperature for lead sulfide.

Sample	Type	Type	$n, 10^{17} \text{ cm}^{-3}$
1	natural, polycrystalline	n	7.5
2	natural, single crystal		5.9
3	natural, polycrystalline		7.5
4	natural, single crystal		.85
5	synthetic, single crystal	p	.17
6	synthetic, Ag-doped, single crystal	"	.018

[Ref. 285]



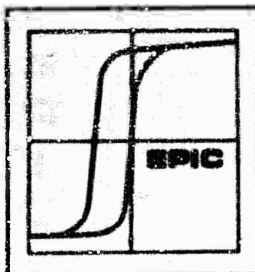
LEAD SULFIDE

THERMOELECTRIC PROPERTIES

Sample	Thermoelectric emf $\alpha$ , $\mu\text{V}/^\circ\text{C}$	Conductivity at 20-300°C $\sigma$ , $\Omega^{-1}\text{cm}^{-1}$	$n$ , $10^{18}\text{cm}^{-3}$ (300°K)	$\text{cm}^2/\text{eV sec}$ (300°K)
n-type, single crystal material used in preparation of film	-186	650	7.5	540
Monocrystalline layers epitaxially deposited, no sensitivity	+137 p-type -245 n-type	30	1.7	110
Polycrystalline layers unsensitized	-188	1.6	10.8	0.93
Sensitized by heating to 600°C in air; films 1 micron thick	+112 p-type -148 n-type	.01	.037	1.7

The unsensitized polycrystalline layer shows the same thermal emf as single crystal material, although conductivity and mobility are greatly reduced due to crystallite volume increase. The absorption of oxygen, however, sharply decreases the conductivity because of decrease in current carriers while mobility remains fairly constant. The thermal emf, does not change so radically and is therefore dependent on volume of crystallites and the diffusion of charge carriers through them.

[Ref. 16371]



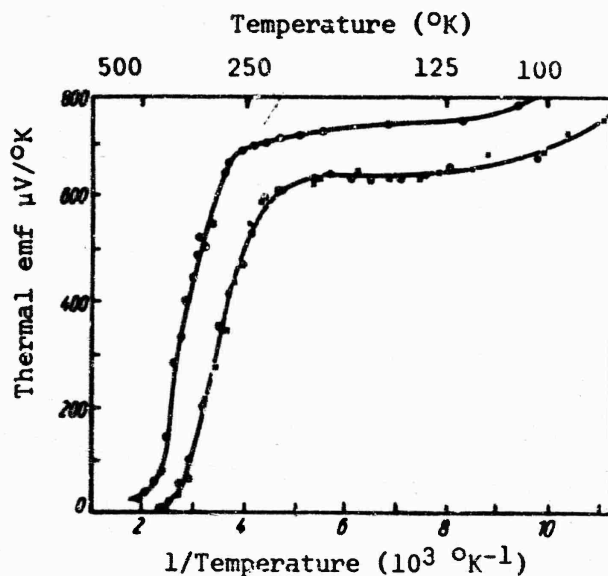
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**LEAD SULFIDE**

**THERMOELECTRIC PROPERTIES**

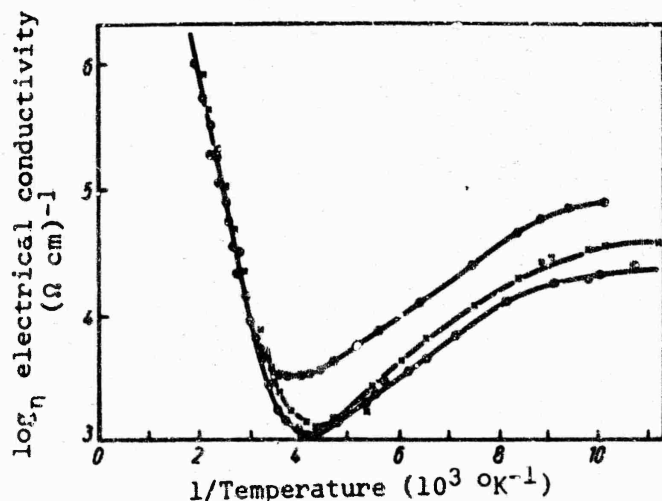
Thermal emf as a function of reciprocal temperature for natural, pure single crystal lead sulfide.

Symbol	$n, (10^{15} \text{ cm}^{-3})$	$\rho_{300^\circ\text{K}} (\Omega \text{ cm})$
●	3.5	2.86
○	1.7	3.29
x	2.1	2.94



[Ref. 19724]

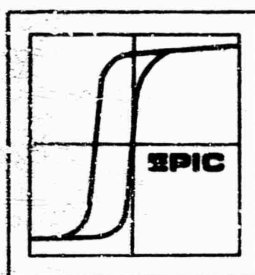
In single crystal material, decrease in temperature is accompanied by a phonon drag effect, the charge carriers are scattered by acoustic phonons. The rise in thermal emf below room temperature reflects the increase in mobility with the decrease in temperature.



Log electrical conductivity as a function of reciprocal temperature for the same samples as shown above.

[Ref. 19724]

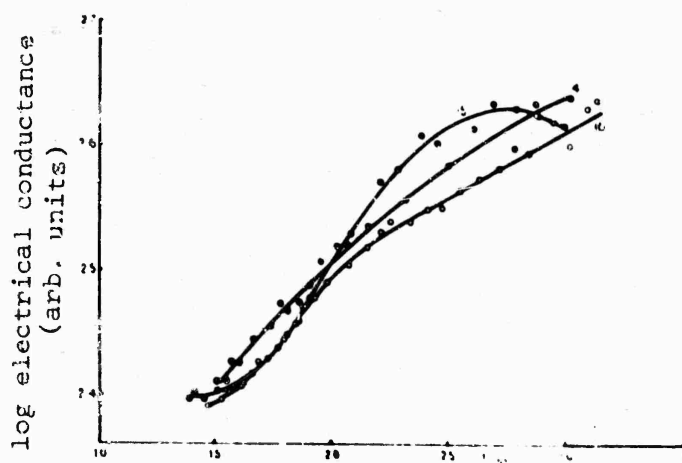
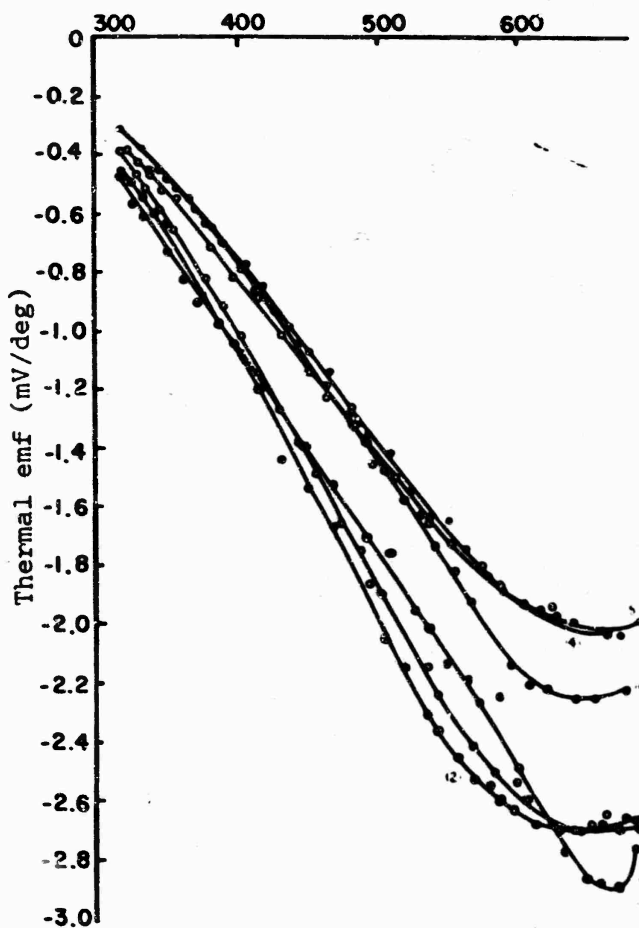




# LEAD SULFIDE

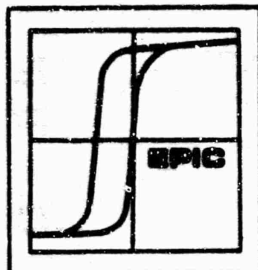
## THERMOELECTRIC PROPERTIES

Thermal emf as a function of temperature for natural single crystal lead sulfide. This is on a metallic n-type sample (excess lead). The curve numbers indicate consecutive runs.



Log conductance as a function of reciprocal temperature for the same sample. The numbered curves correspond to similar numbers on the thermal emf graph. Conductivity on same sample during runs 4, 5 and 6.





# LEAD SULFIDE

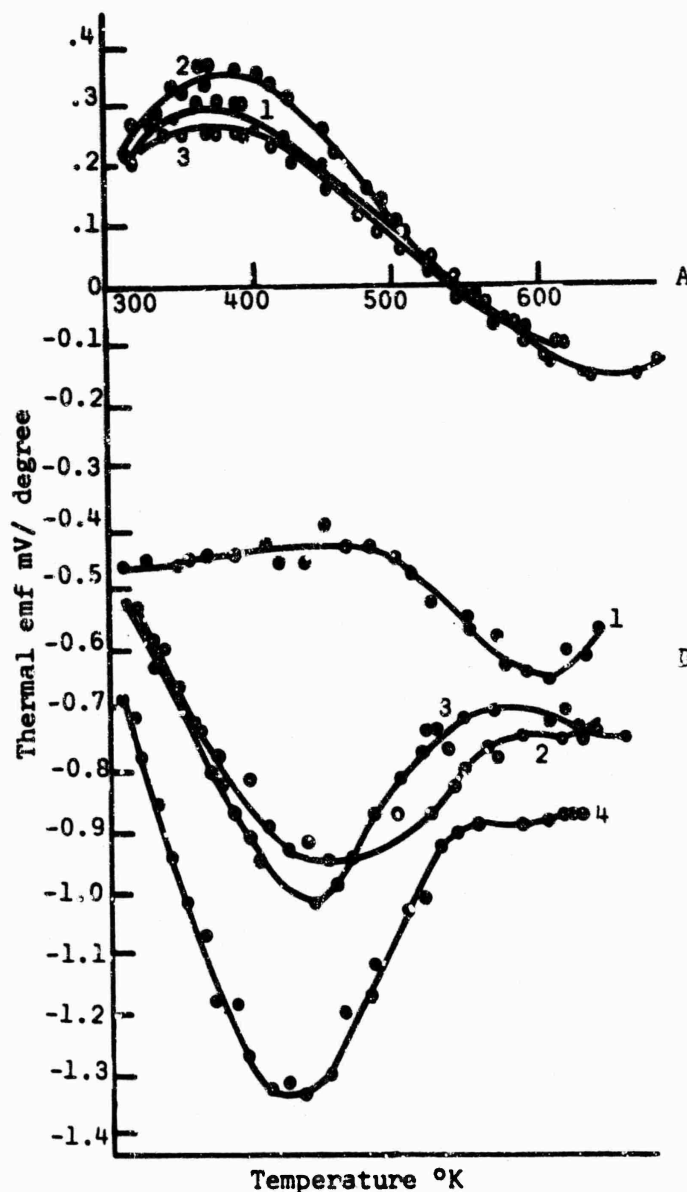
## THERMOELECTRIC PROPERTIES

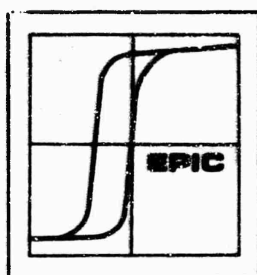
Thermoelectric emf as a function of temperature for natural lead sulfide single crystals.

A) p-type sample. 1, 2, and 3 are consecutive runs, after each of which the sample cools to 300°K.

B) n-type. 1,2,3,4, are similarly consecutive runs.

Heating results in sulfur loss and material becomes increasingly more n-type.

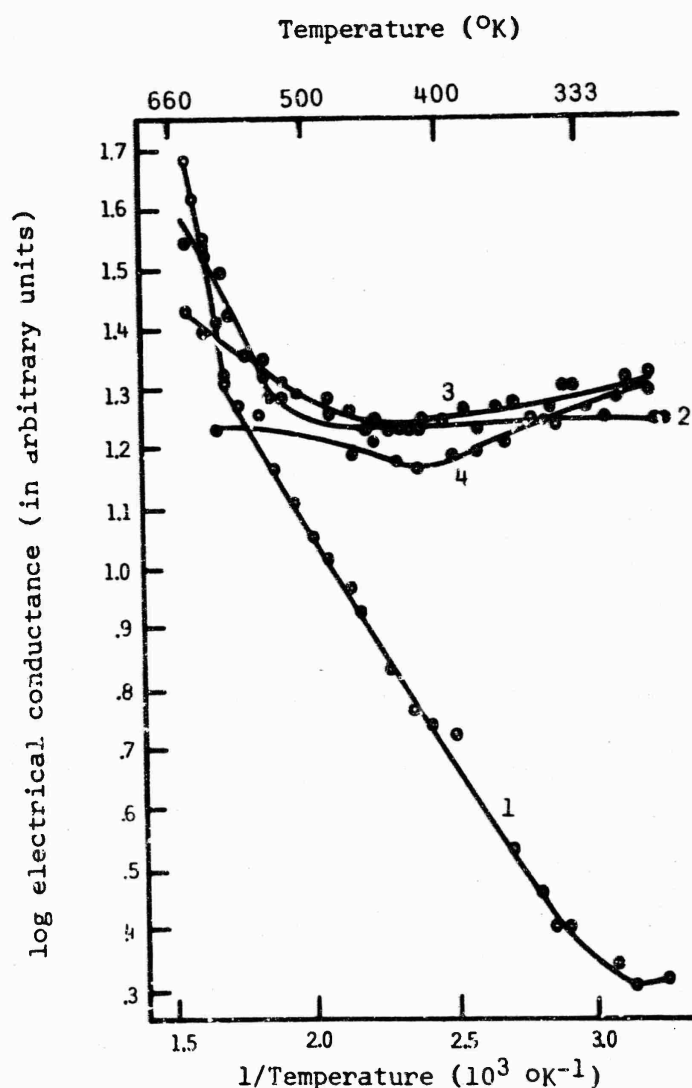




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LEAD SULFIDE

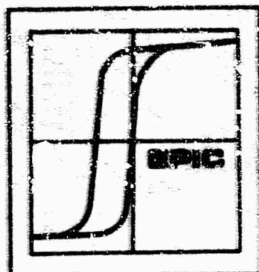
THERMOELECTRIC PROPERTIES



log electrical conductance as a function of reciprocal temperature for n-type sample in graph on preceding page.

Curve 1 shows irreversible change in sample on heating, as a result of sulfur loss.

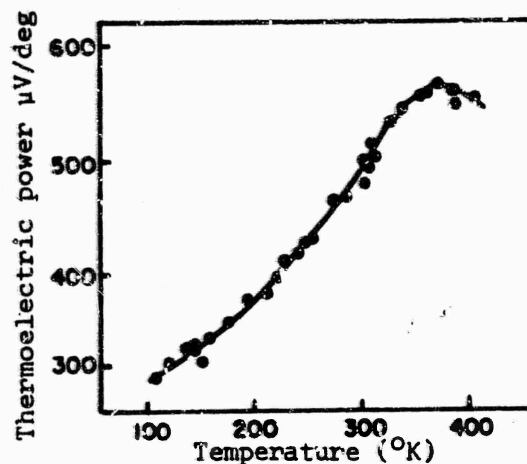
[Ref. 3630]



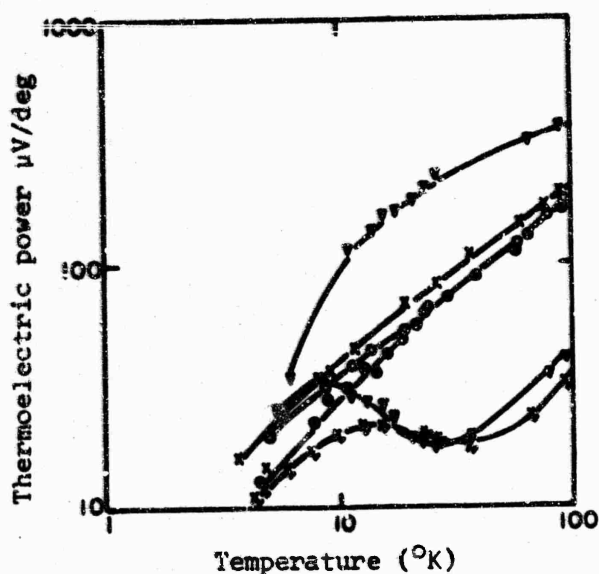
## LEAD SULFIDE

### THERMOELECTRIC PROPERTIES

Thermoelectric emf as a function of temperature for natural single crystals of n-type lead sulfide with  $n = 1.48 \times 10^{17} \text{ cm}^{-3}$ . Peak emf occurs at almost 400°K.



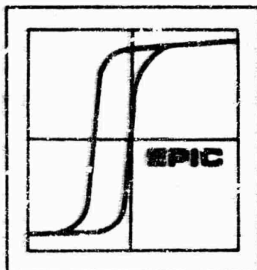
[Ref. 22574]



Thermoelectric emf as a function of temperature for lead sulfide crystals.

Nc.	Type	Sample	$n, 10^{17} \text{ cm}^{-3}$
1●	n	polycrystalline	7.5
2x		single crystal	5.9
3o		polycrystalline	7.5
4*		single crystal	85.
5v	p	single crystal, synthetic	.17
6x		single crystal, (Ag doped)	.018

[Ref. 285]



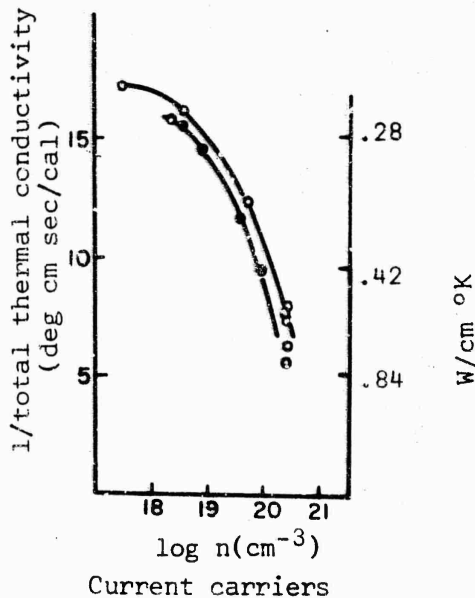
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# LEAD SULFIDE

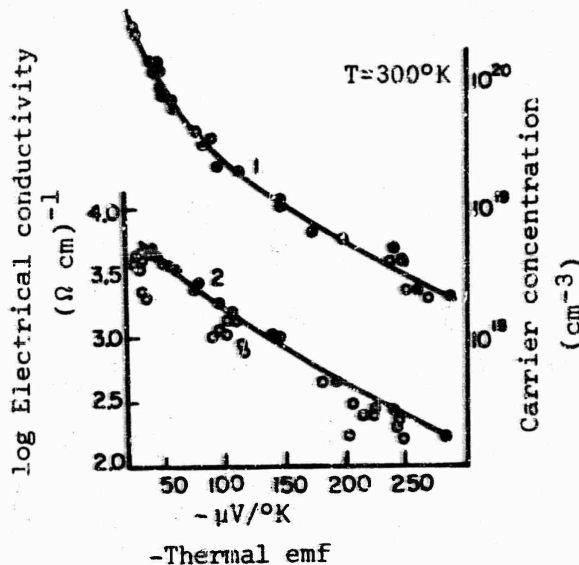
## THERMOELECTRIC PROPERTIES

1) Thermal emf as a function of current-carrier concentration; 2) electrical conductivity as a function of negative thermal emf.

- single crystal
- pressed samples



Reciprocal of the total thermal conductivity as a function of current carrier concentration, for same samples as above.

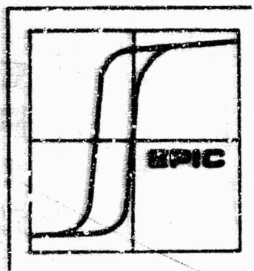


Single crystal lead sulfide is n-type. The pressed samples were prepared by powdering single crystals, and then annealing progressively at  $400^\circ\text{C}$ ,  $650^\circ\text{C}$  and finally at  $300^\circ\text{C}$ . All data taken at  $300^\circ\text{K}$ .

[Ref. 22912]



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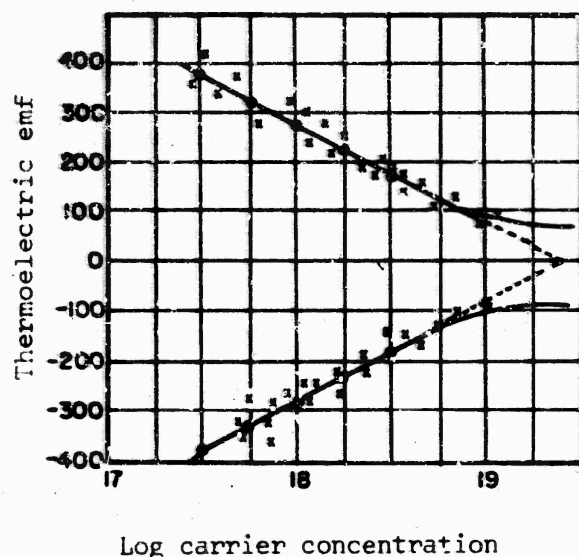


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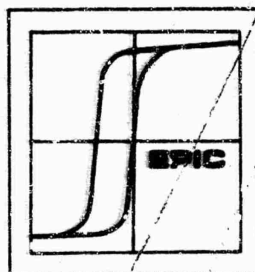
# LEAD SULFIDE

## THERMOELECTRIC PROPERTIES



Thermoelectric emf as a function of log carrier concentration in synthetic single crystal lead sulfide (100) cleavage planes. The carrier concentration is calculated from Hall measurements.

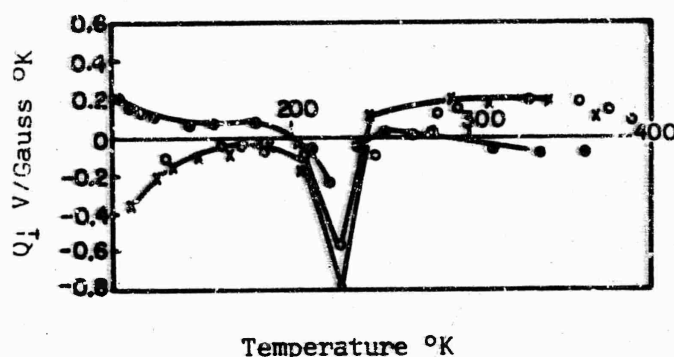
-----calculated for  $m^* = 0.25 m_0$



# LEAD SULFIDE

## THERMOMAGNETIC PROPERTIES

Transverse Nernst-Ettingshausen coefficient as a function of temperature in pure natural single crystal lead sulfide.



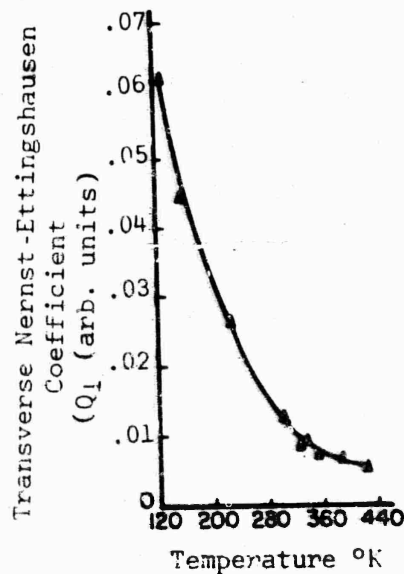
$n, (10^{15} \text{ cm}^{-3})$

$\rho (\Omega \text{ cm}) (300^\circ \text{K})$

$\mu (\text{cm}^2/\text{Vsec})$

[Ref. 19724]

•	3.5	2.86	2600
o	1.7	3.29	2550
x	2.1	2.84	2350

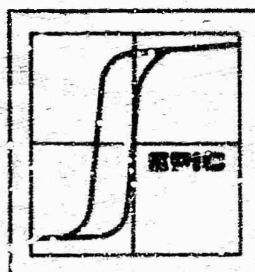


The temperature dependence of the non-dimensional transverse Nernst-Ettingshausen field for single crystal lead sulfide. Sample specimens at 300°K are:

$$\begin{aligned}\sigma &= 450 (\text{ohm cm})^{-1} \\ n &= 6.5 \times 10^{18} \text{ cm}^{-3} \\ \mu &= 430 \text{ cm}^2/\text{V sec} \\ H &= 9200 \text{ Oe}\end{aligned}$$

I.M. Tsidilkovskii. Thermomagnetic Effects in Semi-Conductors. Academic Press. New York (1962) p. 281.

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# LEAD SULFIDE

## WORK FUNCTION ( $\phi$ )

<u>Symbol</u>	<u>Value (eV)</u>	<u>Sample</u>	<u>Test Method</u>	<u>Ref.</u>
$\chi^*$	4.6	Natural galena single crystal (100) cleavage plane (cleaved in air)	electron photoemission in sealed cells	13554
$\phi$	$3.5 \pm 0.2$	single crystal natural galena (100). Cleaved in vacuum.	contact potential difference measurement between lead sulfide and a reference electrode.	20510
$\phi$	$3.3 \pm 0.2$	"	"	"
$\phi$	$3.4 \pm 0.1$	natural single crystal, (100) cleavage surface. annealed in argon atmosphere or ion-bombarded and annealed.	electron photoemission	22709
photothreshold =		"	"	"
$3.8 \pm 0.1$ eV				

\*  $\phi$  is electron affinity

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